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Division of Chemical Science

(IZVESTIYA AKADEMY NAUK SSSR)

(OTDELENIE KHIMICHESKIKH)

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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

IVAN NIKOLAEVICH NAZAROV

(Obituary)

Academician Ivan Nikolaevich Nazarov was born on June 12, 1906, in the village of Koshelevo in the Gorky Region. Having completed the courses at the village school (1917) and the secondary school in Arefino, Nazarov took up a post as village teacher. From 1927 to 1931 he taught in the K. A. Timiryazev Agricultural Academy.

Nazarov's scientific activities began in 1931 in Leningrad State University under the supervision of Academician A. E. Favorsky, and in 1934 he defended his candidate's thesis on the subject "Metal Ketyls of the Aliphatic and Aliphatic-Aromatic Series."

Since 1935 Nazarov has carried out scientific work in the Institute of Organic Chemistry of the Academy of Sciences of the USSR, in which he defended his doctoral thesis on the subject "Acetylene Derivatives. Synthesis of Alcohols of the 1-Buten-3-yne Series and Their Reactions." By Favorsky's method he prepared numerous alcohols of this series, and their varied transformations opened a new, fascinating chapter in organic chemistry. In his laboratory, on the basis of his work on butenyne alcohols, extensive investigations were carried out on allyl, diene, and polyene rearrangements and also work on the mechanism of the hydration and cyclization of butenyne hydrocarbons, which led to the development of a new method for the synthesis of various cyclopentenones.

The discovery by Nazarov of simple methods of preparing previously inaccessible divinyl ketones from butenyne derivatives initiated a new line of work in acetylene chemistry and led to the synthesis of many heterocyclic ketones.

Recently, very extensive investigations on the diene synthesis have been carried out under the direction of I. N. Nazarov. These include very interesting theoretical investigations on the structural orientation of diene synthesis, the stereochemistry of cyclic compounds, and work resulting in the discovery of a new rearrangement of polycyclic ketones having an endomethylene bridge. This group of investigations includes systematic studies on the synthesis of steroids and related substances, and also of isoprenoids.

Nazarov's work has found extensive practical application. Thus, the use of "Carbinol Glue" as a universal adhesive is widely known. During the Great Patriotic War, this glue enabled us to make rapid repairs to military equipment of all kinds. His investigations on heterocyclic compounds resulted in the production of a highly active anesthetic, promedol, which is considerably more active than morphine. Nazarov recently proposed a new method for preparing monomers for the manufacture of synthetic rubber.

I. N. Nazarov has published more than 300 scientific papers.

In 1946 he was elected as Corresponding Member of the Academy of Sciences of the USSR, and in 1953 he became an Academician.

For his outstanding scientific services in the field of organic chemistry Nazarov was twice awarded Stalin prizes. He was awarded also two Orders of the Red Banner of Labor, the Order of the Red Star, and medals for "Defense of Moscow" and "Valiant Labor in the Great Patriotic War, 1941 - 45."

During his years of work at the Institute of Organic Chemistry and the Lomonosov Institute of Fine Chemical Technology, Moscow, Nazarov created a school of synthetic chemistry. Under his supervision

thirty scientific workers defended their Candidate's theses and four became Doctors of Chemistry. Nazarov's students are developing his ideas in the Academies of Sciences of the Republics - in Minsk, Vilna, Erevan, Alma-Ata, the West-Siberian Affiliated Institute of the Academy of Sciences of the USSR, and in other places. I. N. Nazarov was elected as a member of the German Leopold Academy of Naturalists and as Corresponding Member of the German Academy of Sciences in Berlin.

In the person of I. N. Nazarov, Soviet science has lost one of the most eminent scientists, who was unreservedly devoted to science, and whose activities were wholly directed to the development of Soviet organic chemistry.

The image of I. N. Nazarov— the communist-scientist— will ever remain with us in our hearts as an example of unbounded love of science and of his work.

Ivan Nikolaevich Nazarov

CORROSION OF SILICATE GLASSES BY ALKALINE SOLUTIONS

COMMUNICATION 1. BREAKDOWN OF QUARTZ, QUARTZ GLASS, AND SOME LABORATORY GLASSES BY SODIUM HYDROXIDE AND SODIUM CARBONATE SOLUTIONS

V. S. Molchanov and N. E. Prikhidko

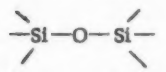
Alkaline solutions have an appreciable destructive effect on natural silicates and on manufactured silicate materials, in particular, glasses, their destructive action being exceeded only by that of hydrofluoric acid. In all kinds of preparative work, in precise analytical determinations, and in the operations of cleaning and degreasing the surface of glass apparatus, it is important to know the susceptibility of the particular glass to the action of alkaline solutions. The problem of stability to alkali forms a little-studied aspect of the corrosion of silicate glasses. Not only do various chemical phenomena occurring during the alkaline breakdown of glasses remain unexplained— e.g. "soda paradoxes" or the phenomenon of corrosion inhibition [1]— but erroneous views are widespread concerning the alkali-stability of the glasses with which physicists and chemists are constantly dealing in the laboratory. In particular, many incorrectly regard the thermally stable glass Pyrex as also highly stable chemically. A fairly prevalent view is that the best available glass for work with neutral and acid solutions is quartz glass, although it is inferior to many other glasses in its resistance to alkalis, and that complex silicate glasses are attacked by these substances to an extent that is directly proportional to the silica content. Data in recent literature, and also the data presented below, do not support these views. It is only quite recently that a group of glasses (zirconium-containing) has been discovered with alkali-stabilities equal to, or even greater than that of quartz glass [2]. In most cases, however, quartz glass remains a material of very high chemical stability among silicate glasses.

At the basis of the destructive action of alkaline solutions on silicates lies the passage of silica into the soluble condition, which, in the case of quartz glass, can be conventionally represented as:

$$SiO_2 + 2NaOH \rightarrow SiO_3'' + 2Na + H_2O.$$

Alkalis have the same action also on the polymeric silicon-oxygen anions entering into the composition of crystalline silicates and glasses, i.e. bring about their depolymerization and passage into solution in the form of relatively simple ions. In this process the cations of the glass form either hydroxides or silicates that are simpler in composition and are more highly hydrated than the silicates present in the original glass.

Views on the kinetics of the breakdown of glasses by alkaline solutions were developed by Berger and Geffcken [3], who considered that the action of alkali on silica begins with the adsorption of NaOH on its surface, an unstable compound being formed. The formation of this adsorption compound is rapid, requiring not more than one-thousandth of a second. This compound then breaks down with rupture of



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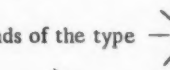

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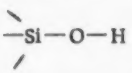
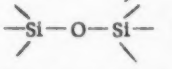


in place of each original link. Breakdown of sufficient



links results in complete breakdown of the crystalline lattice of the silicate— or of its equivalent in the case of glasses— and consequent passage of the broken-down material into solution. The breakdown of the adsorption com-

pound is a slow process, requiring but one second, according to Berger and Geffcken's estimate. The rate of this stage determines the rate of the breakdown process as a whole, and the specific effects of temperature, concentration, and stirring of the solution on the corrosion of glasses are also dependent on this stage.

Owing to the appreciable solubility of the corrosion products— hydroxides and silicates— when considered in relation to the small absolute amount of glass attacked, the final result of the action of the alkaline solution is complete removal of substance from the surface down to a definite depth without formation of a residual protective layer of breakdown products, such as is formed in the action of acids or water [1]. Only in the corrosion of highly unstable glasses, when attacked to a depth of several microns, is the formation of an incrustation of hydrated silicates, carbonates, and other salts observed, though this does not retard further attack owing to its open structure. The alkali-stability of a glass, therefore, can be characterized accurately by the amount of glass dissolved. For the determination of this amount, use has been made in the past of gravimetric methods, either based on measurements of the loss in weight of the glass in the form of a piece of tubing, a flask, a plate, or powder, or based on determination of the weight of dry residue obtained on evaporation of the reagent used for the treatment of the glass. The low accuracy with which the very small loss in weight of samples of low specific surface can be measured, the phenomenon of "poisoning" of the reagent by breakdown products in the case of glass powders*, and the enormous correction for the value of the dry residue of the reagent itself all make it preferable to adopt the methods, based on interferometry, used for the measurement of the alkali-stability of glasses in 1935 by workers at the National Bureau of Standards (US) [5] and later by other workers. The only difficulty in the application of this method— the lack of availability of interferometers— has now been removed. Thanks to the efforts of the school of Academician V. P. Linnik, Soviet science has been enriched by several interferometers [6] of Soviet manufacture which are available for the ordinary laboratory. These include the microinterferometer IZK-46 and the interference microscopes MII-1 (high-precision) and MII-5 (simplified version). Although these instruments are intended mainly for the study of the highly reflecting surfaces of metals, they may be used without modification for the study of glass surfaces. If to these instruments we add Linnik's double microscope MIS-11, then we have the means of measuring the depths of breakdown of glass over a very wide range— 0.03-60 μ— which more than covers the range of values with which we are concerned in the investigation of the alkali-stability of glasses.

These considerations prompted us to use the interference microscope MII-1 and the double microscope MIS-11 (for very highly corroded glasses) and determine with their aid the degree of breakdown brought about by alkaline treatments in quartz, quartz glass, and some laboratory glasses.

EXPERIMENTAL

The determination of the alkali-stability of glasses by the interferometric method amounts to the measurement of the thickness of the layer of glass dissolved by the alkaline solution by estimating the degree of distortion of the interference bands observed when the glass surface is examined in the interferometer. The bands are distorted at the boundary between the corroded and uncorroded sections of the glass surface. We obtained such a boundary by clamping polished (accurately within 2 — 1/2 bands) glass plates (20 × 20 × 10 mm) between two silver plates which could be drawn together by means of two silver screws (Fig. 1). Interlayers of soft rubber were placed between the glass and the silver plates. The samples were clamped so that a narrow strip of the surface, parallel to the edge of the clamp and about 0.5 cm^2 in area, was exposed below the interlayer. This exposed strip was subjected to the action of the alkaline solution. The assembly was placed in a silver beaker contained in an ultrathermostat that maintained the temperature constant within 0.1°. The appropriate alkaline solution (950 ml) was previously heated in the beaker. A rod fixed to one of the silver plates of the clamp was coupled with the shaft of a motor, so that the clamp itself could act as a stirrer. The motor was run at 200 r.p.m. In order to prevent evaporation of the water, the beaker was covered with a transparent plastic disc having a central hole to take the rod carrying the clamp. After the necessary time, the clamp was removed from the solution,

* This phenomenon, specific for the breakdown of glasses by alkaline solutions, was described by Geffcken [4].

Fig. 1. Clamp for glass samples.

washed with water, and dismantled. The glass sample was wiped with a clean cloth and examined with the MII-1 microscope or the MIS-11 double microscope. The use of rubber interlayers did not guarantee an ideally sharp, perpendicular boundary between the attacked and unattacked portions of the surface. Sometimes a sloping boundary was obtained, and in some cases a groove was formed [1]. This disturbed the regular formation of interference bands and made measurement difficult. We succeeded in obtaining reliable measurements of corrosion proceeding to depths of 0.08-0.1 μ and more. In the MII-1 microscope the upper limit of measurements could be extended to 8 μ. The general reproducibility of measurements can be judged from the following examples. In the determination of the thickness of the dissolved layer at six points of the boundary on one glass plate we obtained the values 1.20, 1.25, 1.34, 1.40, 1.20, and 1.30 μ, or on the average 1.28 μ with a relative error of ± 5.0%. The value of the dissolved thickness of the dissolved layer for different samples of glass from the same melt was reproduced accurately within ±10%.

Taking into account the known lower limit of measurement, we selected a suitable temperature and concentration of reagent to allow us to obtain measurable values for the breakdown of quartz glass— a plate of Soviet optical quartz. As a matter of practical convenience, the duration of the experiment was fixed at four hours. The temperature used was such that an appreciable thickness of the glass was dissolved in this time. Table 1 gives the results of experiments at different temperatures for corrosion by 0.5 N NaOH.

TABLE 1

Temperature (°C)	Thickness of dissolved layer (μ)	Rate of corrosion (μ/hour)
50	0.03	0.007
60	0.12	0.025
70	0.20	0.050
80	0.40	0.100
90	0.80	0.200
94	0.94	0.235
97	1.10	0.275

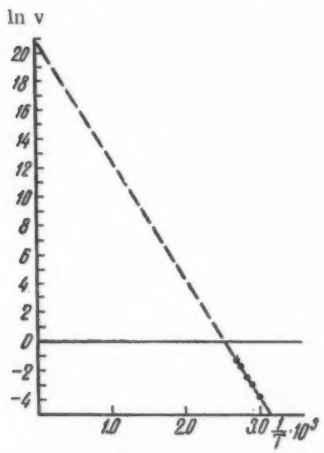


Fig. 2. Relation of the logarithm of the rate of corrosion of quartz in 0.5 N NaOH to temperature $\ln v = -\frac{8225}{T} + 21$ (equation to straight line).

As can be seen from Table 1, in accord with data in the literature, the rate of corrosion of glass by alkalis is greatly affected by temperature. Each ten-degree rise in temperature approximately doubles the rate of corrosion. As the standard temperature of the experiments we selected 90°, which guaranteed sufficiently great, reliably measurable thicknesses of corroded layers.

When the data in Table 1 are plotted in the form of logarithm of the rate of corrosion against the reciprocal of the absolute temperature (Fig. 2), a straight line is obtained with a slope characterizing the activation energy Q for the processes of breaking down quartz glass with alkali:

$$\tan \alpha = \frac{26 \cdot 10^3}{3.16} = 8225;$$

$$Q = 2.303 \cdot 0.002 \cdot 8225 = 37.81 \text{ kcal/mole}.$$

Calculation gives a value of 38 kcal/mole, which is considerably higher than that given in the literature [3] for complex glasses (about 18 kcal/mole). The high activation energy indicates the high stability of quartz glass toward alkalis. At the chosen duration (4 hours) and temperature (90°) of the experiments, we studied the effect of the alkali concentration in the range 0.01-10 N on the depth of corrosion. The results are given in Fig. 3. They indicate that from 0.5 N upward the extent of corrosion is proportional to concentration. This simple relation made it possible to take 0.5 N NaOH, which is convenient also for practical reasons, as our standard reagent.

The constancy of rate of corrosion was checked under the selected experimental conditions. It is known that constancy of rate of corrosion is a characteristic feature of the

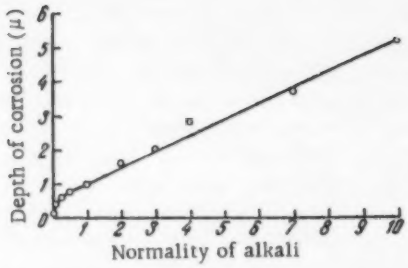


Fig. 3. Relation of depth of corrosion of quartz glass to concentration of NaOH (4 hours, 90°).

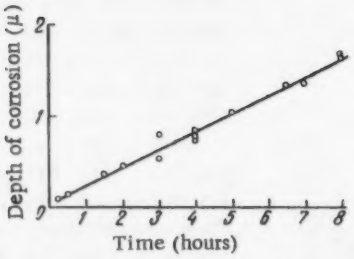


Fig. 4. Relation of depth of corrosion of quartz glass by 0.5 N NaOH to time (90°).

breakdown of glasses by alkalis and distinguishes this process from breakdown in neutral and acid solutions, when a protective film is formed on the glass surface. As Fig. 4 shows, the conditions of our experiment adequately ensure absence of poisoning, and even when the duration of the immersion of the glass in alkali was increased to eight hours, the proportionality of the thickness of the layer of dissolved glass to time was preserved.

Breakdown of Quartz and Various Glasses in Alkalis. We determined the rates of corrosion under standard conditions of crystalline silica (rock crystal), optical quartz glass from three different works, and eleven multicomponent glasses. These last included the well-known Tishchenko glasses [7] ("Druzhnaya Gorka" [DG] No. 23 and No. 24, which have been used for about fifty years for the manufacture of laboratory ware), the boron-free substitute for No. 23 (the so-called DG No. 29, devised by a team of workers headed by Evstropyev and Kachalov [8]), the glass Ts-32, which contains 3.5% of zirconium dioxide and has been used in recent years for the manufacture of chemical glassware in the Laborpribor works, and finally Pyrex laboratory glass. We investigated also electrovacuum glasses that are widely used in the construction of apparatus for physical investigations (No. 46, molybdenum, and No. 17, Nonex) and L-100 glass, which has recently found wide application in the manufacture of vacuum apparatus. We also estimated the corrosion of two zirconium-rich glasses Ts-18 and Ts-21, which are intended for the manufacture of water gages for boilers and were developed by a team of workers directed by Botvinkin [2]. These glasses are unique with respect to alkali-stability, and it was of interest to compare their behavior with that of other glasses. Finally, we measured the corrosion of the so-called MacInnes glass, which is used for making glass electrodes [9].

Not only 0.5 N NaOH, but also 0.5 N Na_2CO_3 and a mixture of equal volumes of these solutions were taken as reagents (this mixture is used in some countries as a standard reagent for the testing of glasses, enamels, etc.). Table 2 gives the thicknesses of dissolved layers obtained in four hours and also the reciprocals of rates of corrosion, which can be taken arbitrarily as measures of chemical stability.

It will be seen from Table 2 that the stability of crystalline quartz is several times as high as that of quartz glass. This superiority of crystalline quartz provides further proof of the great store of internal energy in glasses in general, as compared with the crystal of the same composition*, which must be regarded as a consequence of the non-equilibrium nature of the glass state, in which the excited states of the bonds between atoms and the disordered spatial arrangements of the atoms are fixed.

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* The high stability of matter in the crystalline state, as compared with that of the glass of the same composition, is proved by our experiments with the mineral jadeite. Under standard conditions the thickness of the dissolved layer of the mineral is less than 0.03 μ, whereas synthetic jadeite glass was dissolved by 0.5 N NaOH to a depth of 2.01 μ.

TABLE 2

No.	Glass	Depth of corrosion (μ) under the action of			Stability, expressed as reciprocal of rate (hours per 1 μ)		
		NaOH	Na_2CO_3	NaOH + Na_2CO_3	NaOH	Na_2CO_3	NaOH + Na_2CO_3
1	Crystalline quartz	0.03	0.03	0.03	133	133	133
2	Clear fused quartz from the Lomonosov works	0.8	0.3	0.7	5	13.3	5.9
3	Clear fused quartz from the optical works	0.5	0.3	0.5	8	13.3	8.0
4	Clear fused quartz from the firm of Hereus (W. Germany)	0.7	0.4	0.52	5.9	10.0	8.0
5	Laboratory glass DG-23	1.6	1.5	1.6	2.5	2.7	2.5
6	Laboratory glass DG-24	1.2	1.1	1.1	3.3	3.6	3.6
7	Laboratory glass DG-29	1.3	1.4	1.3	3.1	2.9	3.1
8	Laboratory glass Ts-32	0.9	0.7	0.7	4.4	5.0	5.0
9	Pyrex laboratory glass	7.3	5.3	6.1	0.5	0.7	0.6
10	Molybdenum No. 46	7.6	3.3	6.5	0.5	1.2	0.6
11	Nonex (No. 17)	14.9	23.9	11.3	0.3	0.1	0.3
12	L-100	8.6	9.1	10.5	0.5	0.4	0.4
13	Zirconium Ts-18	0.2	0.3	0.2	20	13.3	20.0
14	Zirconium Ts-21	0.1	0.1	0.1	40	40	40
15	MacInnes glass	2.4	3.7	3.8	1.7	1.1	1.1

Quartz glass manufactured at different works has almost the same stability to the action of alkalis. The laboratory glasses No. 23, 24, 29, and 32 are almost identical in alkali-stability, though the glass Ts-32 is to be preferred somewhat to the others, the presence of zirconium being a powerful factor tending to increase alkali-stability. This fact becomes particularly clear from data on the glasses Ts-18 and Ts-21, which are corroded considerably more slowly than quartz glass. We do not know of any other cases in which the stability of a complex silicate glass is higher than that of fused quartz.

The group of glasses rich in boron (Pyrex and electrovacuum glasses) are considerably less stable to alkalis than the remainder. Pyrex, therefore, should not be used for the fabrication of apparatus intended for experiments with aqueous solutions in which contamination with the breakdown products of the glass is undesirable.

Glass for the fabrication of glass electrodes occupies an intermediate position, but is by no means one of the worst glasses, a fact that is very interesting when it is remembered that it contains 22% of sodium oxide. It would appear, therefore, that in the development of this glass a very satisfactory composition was found, giving a glass having the necessary electrical characteristics with adequate chemical stability.

When the effects of the different reagents are compared it is found that only in the case of glasses No. 17 and L-100 is the action of the sodium carbonate solution or of the mixed solution stronger than that of the sodium hydroxide solution (the so-called "soda paradox" [1]). In the case of the other glasses this phenomenon was not observed. The question of the soda paradox and of the relation of alkali-stability to composition will be examined in detail in our future communications.

SUMMARY

1. Suitable treatment conditions were chosen so that the depth of corrosion of silicate glasses by alkaline solutions could be determined with the aid of the MII-1 interference microscope (the measurements being accurate within not more than ±10%).

2. It was shown that the depth of corrosion of quartz glass is proportional to the duration of treatment and to the concentration of the alkaline solution. With rise in temperature, the depth of corrosion increases in accordance with an exponential law (it is approximately doubled for each 10° rise in temperature).

3. The alkali-stabilities of fifteen technically important glasses were determined under the chosen conditions. Quartz and zirconium-rich glasses were the most stable. Crystalline quartz is more than ten times as stable as quartz glass.

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Institute of Silicate Chemistry of the Academy of Sciences of the USSR

*In Russian.

PHYSICAL AND CHEMICAL PROPERTIES OF WS_2 CATALYSTS

COMMUNICATION 1. EFFECT OF THERMAL TREATMENT ON THE COMPOSITION AND ADSORPTION PROPERTIES OF WS_2 OBTAINED BY THE DECOMPOSITION OF AMMONIUM THIOTUNGSTATE

S. M. Samoilov and A. M. Rubinshtein

Tungsten sulfide has been used successfully during the last twenty-five years as an industrial catalyst for the destructive hydrogenation of heavy hydrocarbons. In various papers and patents detailed descriptions have appeared of the conditions required for the hydrogenation of complex mixtures and individual compounds, and also of the composition and properties of the products. Unfortunately, very few papers have appeared which are concerned with the detailed investigation of the WS_2 catalysts themselves and, in particular, with the determination of their specific surface and porous structure.

It is stated in the literature that the catalytically active form of WS_2 is obtained by the decomposition of ammonium thiotungstate $(NH_4)_2WS_4$. For the production of catalysts, it is now usual [1, 2] to carry out this decomposition in a stream of hydrogen at 400°. The reaction occurring is represented only approximately by the equation

$$(NH_4)_2WS_4 + H_2 = WS_2 + (NH_4)_2S + H_2S \qquad (1)$$

since the tungsten sulfide formed generally contains excess of sulfur. The specific surface of the WS_2 catalyst obtained by reaction (1) was determined by Pier [2] by adsorption of argon, and by Friz [3] by adsorption of CO_2 and SF_6; they found it to be 20 sq. m/g. According to Pier [2], the relative pore volume of a single tablet of catalyst was 50%. Adsorption of CO_2 was carried out [3] at −78°, and the specific surface was calculated by the BET equation. The conditions under which adsorption of argon and SF_6 occurred and the method of calculating specific surface in these cases is not indicated. Moreover, neither author describes the methods he used for the preliminary treatment of the catalyst and degassing of its surface before the adsorption measurements. We must point out that the adsorption isotherms are not given, so that these results must be regarded as merely provisional. Kalechits, Pavlova, and Samoilov [4] studied the adsorption of nitrogen at the temperature of liquid nitrogen on a WS_2 catalyst that had been in use, and they found that the catalyst, which had lost its activity, had only about one-half of the specific surface, and one-half of the pore volume of an active catalyst.

The results that we have referred to above, together with some x-ray results, comprise, as far as we know, the whole of the existing information on the physical structure of WS_2 hydrogenation catalysts. In assessing these results, we must remember that it is extremely doubtful whether all the WS_2 catalysts had the same specific surface, irrespective of the conditions of carrying out reaction (1) and their further treatment. Moreover, an undoubted gap in this information is the absence of data on the change in the specific surface of WS_2 catalysts with thermal treatment, and the absence of more detailed data on their porous structure. The fact that the catalyst obtained by reaction (1) generally contains excess of sulfur (W : S = 1 : 2.2 −2.3) makes such data all the more interesting. It may be recalled that a completely analogous phenomenon is observed in another case: excess of sulfur is present also in an MoS_2 catalyst [5], which is isomorphous in its crystalline structure and similar in its catalytic properties to WS_2.

The significance of the excess of sulfur for the catalytic activity of WS_2 and MoS_2 has not yet been elucidated; neither has the variation in surface area and porosity with change in the extent in the departure from the stoichiometric composition, i.e. from the composition $WS_{2.00}$. All that is known is that heating of MoS_2 to 800-1000°, i.e. to temperatures much higher than the hydrogenation temperature for these catalysts, results in reduction of the excess of sulfur [5,6]; at the same time, crystal size increases (this has been noted both for WS_2 and for MoS_2) [2, 6, 7], and there is a loss in catalytic activity [6, 8]. Kingman [6] considers that, as a result of increase in crystal size in the heating of an active MoS_2 catalyst, its specific surface diminishes.

In order to elucidate various obscure questions noted above, we undertook a detailed investigation of the structure of WS_2 catalysts and its effect on catalytic activity. The present paper describes the results of a study of the changes in adsorption properties and chemical composition occurring during various thermal treatments of WS_2 catalysts obtained by reaction (1) and having the composition $WS_{2.30}$. The catalyst samples were heated at various temperatures, ranging up to 1000°, and their chemical compositions and the adsorption of nitrogen at the temperature of liquid nitrogen were then investigated. Some of the samples investigated were examined also for their catalytic activities for the hydrogenation of benzene.

EXPERIMENTAL

With the exception of sample 1_{300} (here and below the numerical subscript to the number of the sample indicates the temperature of treatment), all the samples investigated were prepared from separate portions of the same active WS_2 catalyst (described as No. 3) by thermal treatment under various conditions. Sample 1_{300} was also prepared by reaction (1), but by the decomposition of another portion of ammonium thiotungstate.

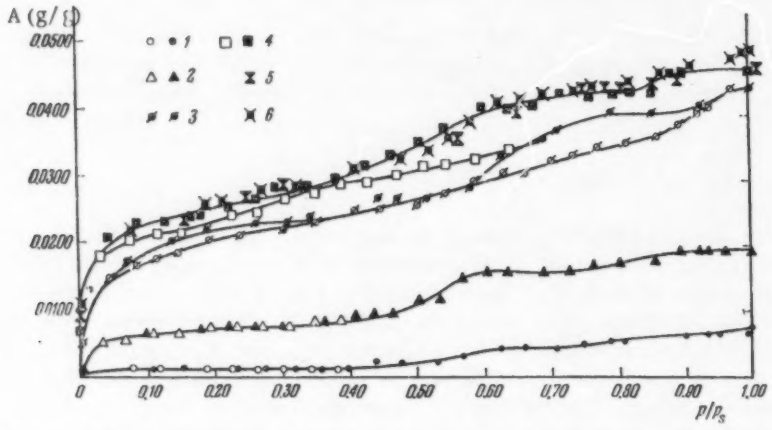

Fig. 1. Adsorption isotherms for nitrogen vapor at the temperature of liquid nitrogen over WS_2 catalysts: 1) 3_{20}; 2) 3_{200}; 3) 1_{300}; 4) 3_{400}; 5) 3_{400} (parallel experiment with another sample); 6) 3_{400} (parallel experiment carried out after the end of adsorption on sample 3_{20} and after heating it at 400° in a vacuum); (black dots—desorption).

One series of samples (3_{20}, 3_{200}, 3_{400}, and 1_{300}) was prepared by heating in a high vacuum, as will be described below. The second series is comprised of portions of No. 3 catalyst heated to higher temperatures (600°, 750°, and 1000°) in an atmosphere of gas; they will be denoted as No. 6, 7, and 8 respectively, and were prepared with the object of determining the effect of overheating the catalyst for short periods, since this matter is of practical interest. As hydrogen reduces WS_2 as low as 800° [9], and the rate of reduction is increased with rise in temperature to 1000° [10], the samples were prepared in a nitrogen atmosphere. Data on their catalytic activities were taken from Pavlova's paper [8] on the hydrogenation of benzene at 400° with an initial hydrogen pressure of 140 atm.

The adsorption of nitrogen was measured gravimetrically in an apparatus of the usual type. The constant of the McLeod gage was $3.2 \cdot 10^{-5}$ mm^{-1}. Cathetometer readings were made accurately within 0.005 mm,

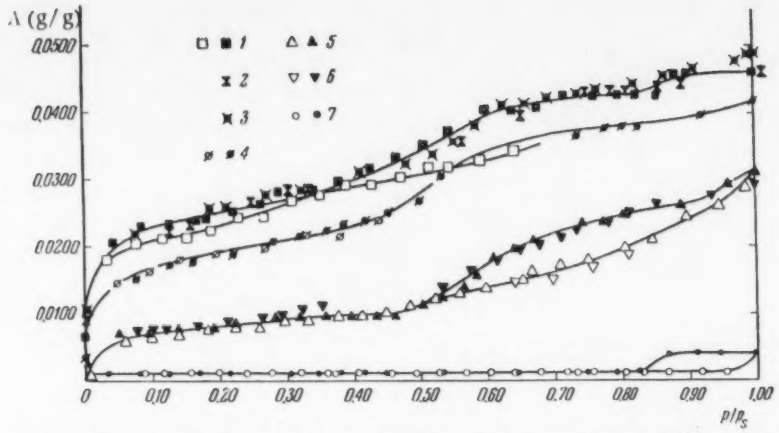

Fig. 2. Adsorption isotherms for nitrogen vapor at the temperature of liquid nitrogen over WS_2 catalysts: 1) 3_{400}; 2) 3_{400} (parallel experiment with another sample); 3) 3_{400} (parallel experiment carried out after the end of adsorption on sample 3_{20} and after heating it at 400° in a vacuum); 4) 6; 5) 7; 6) 7 (parallel experiment with another sample); 7) 8; (black dots— desorption).

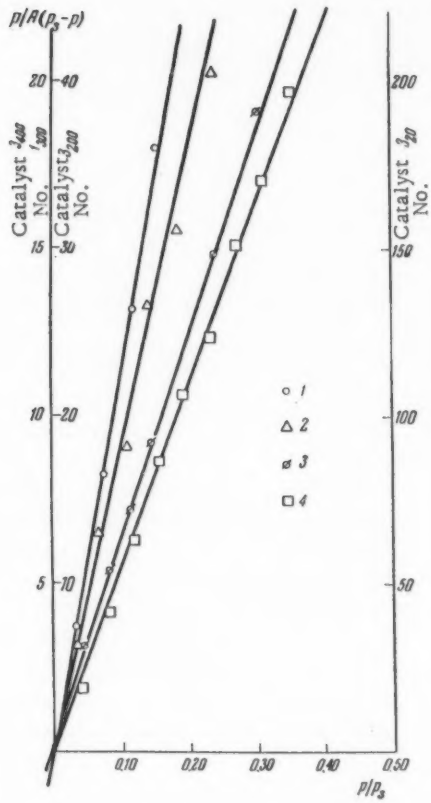

Fig. 3. Application of the BET equation to the adsorption isotherms given in Fig. 1 (the scales for the different samples are indicated on the axis of ordinates): 1) 3_{20}; 2) 3_{200}; 3) 1_{300}; 4) 3_{400}.

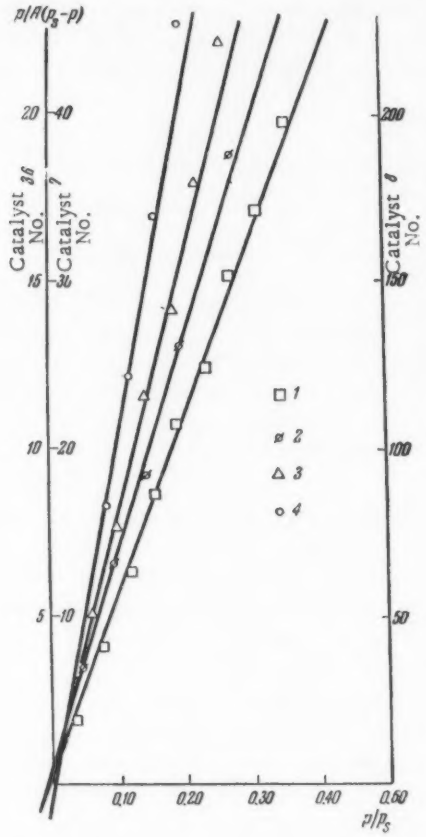

Fig. 4. Application of the BET equation to the adsorption isotherms given in Fig. 2 (the scales for the different samples are indicated on the axis of ordinates): 1) 3_{400}; 2) 6; 3) 7; 4) 8.

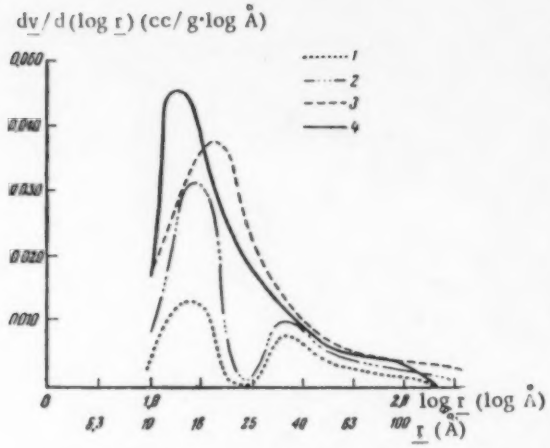

Fig. 5. Distribution of pore volume of WS_2 catalysts with respect to effective radii, calculated from the desorption isotherms for nitrogen vapor given in Fig. 1: 1) 3_{20}; 2) 3_{200}; 3) 1_{300}; 4) 3_{400}

and readings on a U-shaped mercury manometer, accurately within 1 mm. The constant of the quartz spring was 0.0254 g/mm. The nitrogen contained about 0.1% of impurities; it was passed through a purifying system in which CO_2 and water vapor were absorbed by ascarite, calcium chloride, and phosphoric oxide.

A sample of ground catalyst (about 0.3 g) was subjected to a vacuum of 10^{-5} mm, and was then heated (or kept at 20°, in the case of sample 3_{20}) in a vacuum to 200° (sample 3_{200}), 300° (sample 1_{300}), or 400° (sample 3_{400}) at a rate of 200° per hour. At this temperature the catalyst sample was degassed until constant weight was attained (no change in the course of four hours). The vessel was then cooled with liquid nitrogen, and nitrogen was passed in to saturation pressure. The saturation state was maintained for one hour, this being checked by the constancy in weight. Nitrogen was then pumped off, and the catalyst was resaturated with nitrogen. When the weight of the catalyst in the saturation state had been reproduced twice, the desorption isotherm was measured. Before measurement of the adsorption isotherm, the catalyst was again heated in a high vacuum to a constant weight (no change in the course of one hour). For samples 3_{20}, 3_{200}, 3_{400}, and No. 6, adsorption isotherms were measured up to a pressure p/p_s of 0.4-0.6.

TABLE 1

Chemical Compositions of WS_2 Catalysts

Sample	Treatment	Content (%) of				Molecular Composition	
		W	S	C	H	W	S
3	Original	64.02	25.65	0.44	0.69	1	2.30
3_{400}	Heated to 400° in a vacuum	72.28	25.28	0.33	0.00	1	2.006
6	Heated to 600° in nitrogen	69.91	26.19	0.00	0.00	1	2.16
7	Heated to 750° in nitrogen	72.36	25.98	0.22	0.10	1	2.08
8	Heated to 1000° in nitrogen	71.22	25.62	0.00	0.00	1	2.05

The reproducibility of the results was checked in several ways. Thus, after the adsorption measurements had been completed on sample 3_{20}, this sample was heated in a vacuum to 400°, as indicated above, and the desorption branch of the isotherm was determined and found to be identical with the isotherm for the sample 3_{400}. On some samples both adsorption and desorption were measured twice, and for catalysts 3_{400} and No. 7, two samples were investigated in each case. In all experiments good reproducibility of results was obtained (Figures 1 and 2).

The pore volume was calculated from the saturation point, and the specific surface from the BET equation (Figures 3 and 4). The area occupied by one nitrogen molecule was taken to be 16.2 A^2. The distribution of pore volume with respect to radius was calculated from the desorption isotherms by Kelvin's equation, no account being taken of the thickness of the adsorption film (Figures 5 and 6).

In the preparation of samples No. 6, 7, and 8, the heating in a stream of nitrogen was carried out at a rate of about 250° per hour; the samples were maintained at the maximum temperature for 3-5 minutes and then cooled at a rate of about 150° per hour. Before any measurements were made, the catalyst surface was cleaned by heating the samples at 400° in a high vacuum and resaturating with nitrogen, as indicated above. Analysis of the samples

TABLE 2

Pore Volumes and Specific Surfaces of WS_2 Catalysts Calculated from the Adsorption of Nitrogen at the Temperature of Liquid Nitrogen

Sample	Treatment	Total pore volume (cc/g)	Volume of pores of $r_{eff} > 10$ A (cc/g)	Specific surface (sq. m/g)	Degree of conversion of benzene (%) *
3_{20}	Original	0.0088	0.0075	3	
3_{200}	Heated to 200° in a vacuum	0.0229	0.0116	19	
1_{300}	Heated to 300° in a vacuum	0.0544	0.0231	59	
3_{400}	Heated to 400° in a vacuum	0.0568	0.0199	66	90.8
6	Heated to 600° in nitrogen	0.0510	0.0222	54	84.4
7	Heated to 750° in nitrogen	0.0364	0.0239	23	51.2
8	Heated to 1000° in nitrogen	0.0030	0.0017	3	14.0

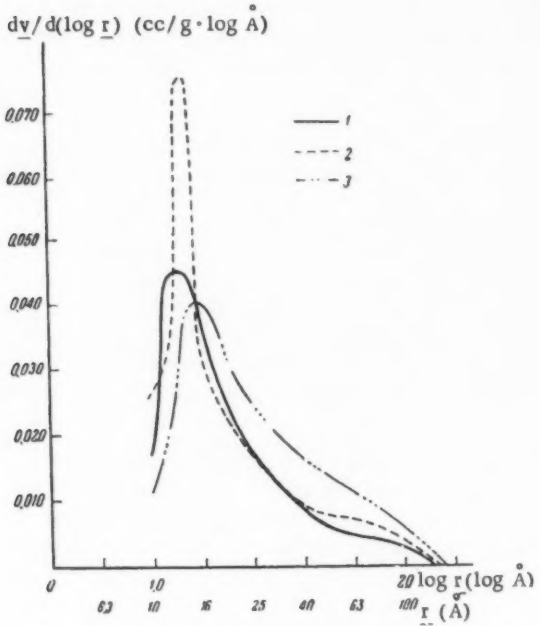

Fig. 6. Distribution of pore volume of WS_2 catalysts with respect to effective radii, calculated from the desorption isotherms for nitrogen vapor given in Fig. 2: 1) 3_{400}; 2) 6; 3) 7.

for W, S, C, and H (Table 1) was carried out in the Analytical Laboratory of the Institute of Organic Chemistry. Samples No. 6, 7, and 8 were analyzed after thermal treatment in a stream of nitrogen, but before degassing in a vacuum ready for further measurements. The results of measurements of specific surface and pore volume are given in Table 2.

DISCUSSION OF RESULTS

As Table 1 shows, the composition of the catalysts investigated is greatly dependent on the conditions of thermal treatment and varies from $WS_{2.30}$ to $WS_{2.006}$. Our experiments have shown, therefore, that both heating in a vacuum and heating in a stream of nitrogen result in reduction in the amount of excess sulfur and approximation to the composition of $WS_{2.000}$: almost complete removal of the nonstoichiometric sulfur is attained by heating in a vacuum at 400°. We observed the liberation of sulfur and its precipitation of the walls of the apparatus at as low as 180-200° in a vacuum. As regards thermal treatment in a stream of nitrogen, heating to 600° at the rate indicated above results in the removal of one-half of the nonstoichiometric sulfur (Catalyst No. 6), and with heating at still higher temperatures (Catalysts No. 7 and 8) this excess of sulfur progressively diminishes. Experiments on thermal treatment in a gas stream showed that excess, nonstoichiometric sulfur is not firmly held in the WS_2 catalyst: when excess of sulfur is present, even brief local overheating can easily result in a change in the composition of the catalyst.

*Data taken from Pavlova's paper [8].

In this paper we shall not examine the question of the form in which the excess of sulfur in the catalyst is present (it has been discussed several times in the literature [2, 5, 6, 11, 12], but has not yet been finally resolved), but we may point out that the excess of sulfur is loosely bound and readily separates in the thermal treatment of the catalyst, particularly during heating in a vacuum. The compound WS_2 is not decomposed under these conditions; this is shown by the results of the analysis of samples 3_{400} and No. 8, and also the analysis of WS_2 after vacuum treatment at 1100° [13].

Removal of sulfur from the catalyst changes its structure. This is most clearly seen in the changes in specific surface and total pore volume brought about by various thermal treatments. These data are given in Table 2; they show clearly that the data on the specific surface of a WS_2 catalyst given in the papers [1] and [2] refer only to a particular case and that the specific surface can vary over a wide range. Moreover, the data in Tables 1 and 2 indicate fairly unequivocally that there is a parallelism between the changes in specific surface and pore volume and the change in the content of excess sulfur, in cases in which complicating sintering processes do not occur. It must be emphasized that the data obtained for Catalyst 1_{300} are in good accord with data for Catalysts 3_{20}, 3_{200}, and 3_{400}, and fit in with the general course of changes observed for this series. The impression is created that the formation and development of the porous structure is a consequence of removal of nonstoichiometric sulfur. For the more detailed examination of our results, which follows below, it is necessary to take account of the distribution of pore volume with respect to effective radii.

The original catalyst, 3_{20}, possesses negligible adsorptive power and a small pore volume, 0.0088 cc/g (Fig. 1, Table 2). Its specific surface, estimated by the BET method, is 3 sq. m/g. Catalyst 3_{20} contains compounds containing hydrogen (0.69 % H, Table 1), which are removed by heat. Nothing more than suggestions have been made concerning the nature of these compounds [2]. In Catalyst 3_{20} pores of effective radius ~15 and ~35 A predominate. When the sample is heated in a vacuum to 200°, the volume of these pores increases. It is interesting that the increase in pore volume is to be accounted for mainly by fine pores of radius 15 A. Correspondingly, Catalyst 3_{200} has a somewhat greater specific surface than 3_{20}. With further heating of the catalyst in a vacuum to 300° and 400°, pores of effective radius 20-30 A make their appearance, the volume of fine pores of effective radius 15 A continues to increase, and ultrafine pores of effective radius less than 10 A make their appearance; for these last the Kelvin equation is no longer applicable, and they are therefore not shown in Fig. 5.

The existence of such ultrafine pores in Catalyst 3_{400} may be inferred on the basis of the following considerations. The adsorption isotherms of Catalysts 3_{200}, 1_{300}, and 3_{400} closely obey the BET equation (Fig. 3), and their specific surfaces, therefore, can be calculated with fair accuracy. When we pass from Catalyst 3_{200} to Catalyst 3_{400}, the specific surface is increased 3.5 times, but the volume of pores of radius greater than 10 A is increased only 1.7 times*. Hence, with increase in temperature of treatment, smaller pores appear; as a result, the catalyst heated in a vacuum at 400° is a finely porous adsorbent with a total pore volume of 0.0568 cc/g, and a specific surface of 66 sq. m/g.

When the catalyst is heated to high temperatures in a stream of nitrogen for a short time and then heated in a vacuum to 400°, adsorption of nitrogen proceeds to a considerably lower extent than in the case of Catalyst 3_{400} (Fig. 2). As compared with 3_{400}, the specific surface of No. 6 is reduced by a factor of 1.2 and the volume of pores of effective radius greater than 10 A is increased by a factor of 1.1 (see Fig. 1 and Table 2). It is clear that in this case increase in order takes place in the crystal structure, and this is associated with elimination of excess of sulfur and increase in the dimensions of elementary crystals. As a result of this process, when Catalyst No. 6 is heated in a vacuum at 400°, the volume of ultrafine pores of effective radius less than 10 A is considerably reduced. On the other hand, there is some increase in the volume of pores of effective radius of ~ 15 A and in the volume of the largest pores of effective radius greater than 50 A (Fig. 6), which probably appear as a result of increase in the size of elementary crystals.

This process occurs to a still greater degree when the catalyst is heated in a stream of nitrogen to 750°. The volume of pores of effective radius less than 10 A is considerably reduced and, on the other hand, the

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*The pore volume can be readily calculated from the characteristic curve $v = f(\log r)$.

volume of the larger pores is increased. The increase in the volume of pores of effective radius greater than 30 A is particularly marked. As a result, in comparison with Catalyst 3_{400}, the specific surface is reduced by a factor of 2.9, and the total volume of pores by a factor of 1.6. Finally, when the catalyst is heated in a stream of nitrogen to 1000°, there is such a great increase in the size of elementary crystals, that the catalyst loses its adsorptive properties almost completely. Our suggested explanation is in close accord with x-ray observations, reported in the literature and also carried out by us, on the increase in the size of crystals in a WS_2 catalyst during roasting. Heating above 600° in a gas stream for a short time results in a considerable reduction in the activity of a WS_2 catalyst, and heating to 1000° almost completely deactivates it. Table 2 shows that the reduction in the degree of conversion of benzene proceeds parallel with the reduction in the specific surface and total pore volume of the WS_2 catalyst.

SUMMARY

1. It was shown that, both when heated in a vacuum and also when heated in a gas at atmospheric pressure, a catalyst of original composition $WS_{2.30}$ loses nonstoichiometric sulfur to an extent that depends on the conditions of heating.

2. It was shown that the specific surface of a WS_2 catalyst varies over a wide range, depending on the conditions of thermal treatment. In the experiments described a 22-fold variation (from 3 to 66 sq.m/g) was found.

3. It was found that there is a parallelism between reduction in the content of nonstoichiometric sulfur during thermal treatment and the increase in specific surface and pore volume, i.e. that the formation of the porous structure of the WS_2 catalyst is associated with removal of nonstoichiometric sulfur. Reduction in specific surface as a result of recrystallization becomes considerable at temperatures above 600°.

4. The distribution of pores was studied by analysis of low-temperature isotherms for the adsorption of nitrogen. The results were examined in their relation to the change in the chemical composition of WS_2 catalysts during thermal treatment.

5. For some of the samples investigated, a comparison was made between structural data and catalytic activity: a parallelism was observed between changes in the degree of conversion of benzene (400°, 140 atm initial pressure) and in the specific surface.

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EFFECT OF TEMPERATURE ON THE RATE OF CORROSION OF METALS

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Knowledge of the rate of corrosion of metals at high temperatures is required in the designing of machines, apparatus, and plants in the chemical, food, and other industries in which metals are subjected to the action of corrosive materials, generally over a wide range of temperatures, in refrigerating systems, steam boilers, steam engines, turbines, and so on.

EXPERIMENTAL

In the present investigation we studied the effect of temperature on the corrosion and electrochemical behavior of iron, copper, zinc, nickel, lead, and magnesium at 0°, 20°, 50°, 80°, and 95° in solutions of 1.0 N NaCl; 1.0 N NaCl + 0.1 N HCl; 1.0 N NaCl + 0.1 N NaOH; and 1.0 N NaCl + 0.1 N $KMnO_4$. The rate of corrosion was determined gravimetrically. The investigation was carried out in vessels fitted with reflux condensers to prevent change in composition of the solution during the tests. In the determination of the rate of corrosion of metals in a "closed system" in which oxygen was not removed from the vessel for the tests, the sample was placed in a glass test tube, diameter 15 mm and length 250 mm, half-filled with solution. The upper end of the test tube was sealed and, to speed up the heating, it was placed in water at 95-98° for ten minutes before being transferred to a thermostat at the required temperature. Electrochemical investigations in a "closed system" were carried out in the apparatus shown diagrammatically in Fig. 1.

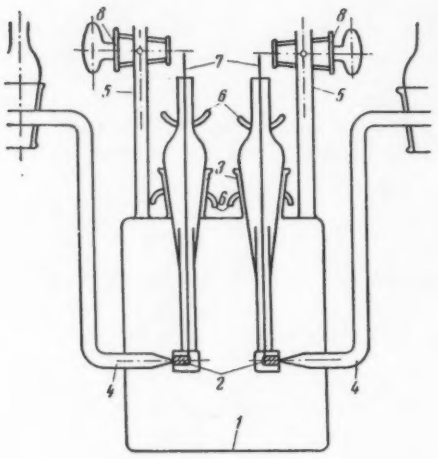


Fig. 1. Diagram of apparatus for the investigation of the kinetics of electrode processes in a "closed system": 1) vessel; 2) samples; 3) ground joints; 4) electrolytic keys*; 5) tubes for filling apparatus; 6) hooks for securing samples in position; 7) leads; 8) taps

Let us examine the way rise in temperature affects the rate of corrosion of metals when the controlling factor is the rate of transport of oxygen. This case includes the corrosion of iron, lead, zinc, and, to some extent, copper (above 50-60°) in a neutral medium, and of lead and zinc in an alkaline medium [1-3]. The rate of diffusion of oxygen increases with rise in temperature. However, owing to the reduction in the solubility of oxygen with rise in temperature, the curves expressing the relation of the rates of corrosion of the above metals to temperature show maxima (Fig. 2 and Table). The limiting diffusion current varies with temperature in a similar way (Fig. 3). It would be expected that in a "closed system" both the limiting diffusion current and the rate of corrosion processes controlled by diffusion would rise continuously with rise in temperature.

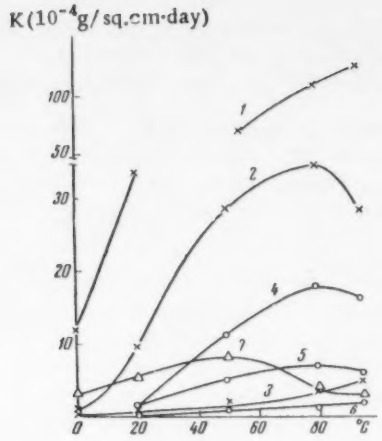


Fig. 2. Effect of temperature on rate of corrosion of metals: 1) Mg in 1.0 N NaCl + 0.1 N NaOH; 2) Pb in 1.0 N NaCl + 0.1 N NaOH; 3) Fe in 1.0 N NaCl + 0.1 N NaOH; 4) Pb in 1.0 N NaCl; 5) Fe in 1.0 N NaCl; 6) Ni in 1.0 N NaCl; 7) Cu in 1.0 N NaCl + 0.1 N $KMnO_4$.

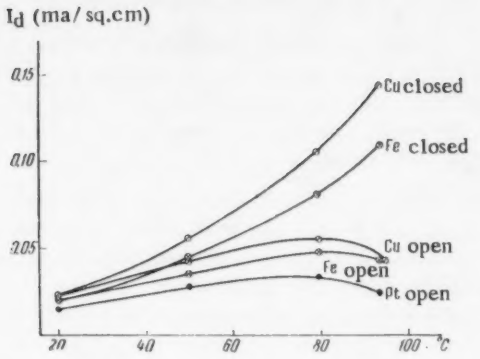


Fig. 3. Effect of temperature on the limiting diffusion current in 1.0 N NaCl: on copper in a "closed system"; on iron in a "closed system"; on copper in an "open system"; on iron in an "open system"; and on platinum in an "open system" .

It follows from Fig. 3 that with constant oxygen content in the system the limiting diffusion current on iron and copper in 1.0 N NaCl rises continuously with rise in temperature. Under these conditions the curve for the relation of the rate of corrosion of copper to temperature does not pass through a maximum (Fig. 4). A similar observation for the case of iron was made by Speller [4].

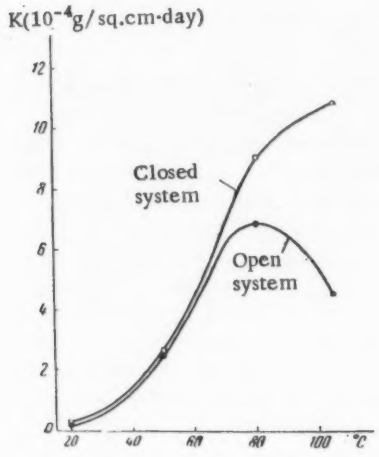


Fig. 4. Relation of rate of corrosion of copper to temperature in 1.0 N NaCl in "closed" and "open" systems .

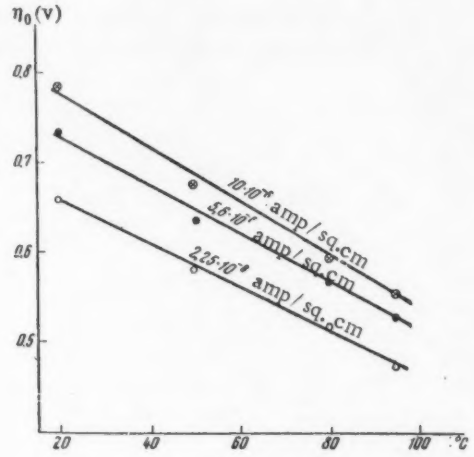


Fig. 5. Temperature-dependence of the overvoltage for the ionization of oxygen at platinum in 1.0 N NaCl .

In a neutral medium the rate of corrosion of nickel, and therefore also the rate of reduction of oxygen, is very small at all temperatures (Fig. 2). As a result, the rate of transport of oxygen to the metal surface is

not a controlling factor; the controlling factor is the rate of ionization of oxygen. Investigation of the kinetics of the cathode process of reduction of oxygen on platinum in 1.0 N NaCl showed that with rise in temperature the overvoltage of the ionization of oxygen diminishes (Fig. 5) to the extent of 2.8 mv per degree, on the average. As a result, there is an increase in the rate of ionization of oxygen, which, in its turn, results in a continuous rise in the rate of corrosion of nickel with rise in temperature (Fig. 2).

Investigation of the kinetics of the electrode processes showed that copper and iron are considerably polarized in an alkaline medium, both cathodically and anodically, from which we may conclude that in this case the corrosion process proceeds with mixed control. With rise in temperature, both the cathodic and the anodic processes become more rapid. These results are in accord with the results of other investigations [1, 3, 5, 6].

In an alkaline medium the rate of corrosion of copper and iron is lower than in a neutral medium (Fig. 2), in which the controlling factor is the rate of diffusion of oxygen. This fact gives us reason to suppose that in the given case corrosion is not determined by the diffusion of oxygen and the cathodic process is determined by the rate of ionization of oxygen. The increase with rise in temperature of both rate of ionization of oxygen and rate of anodic dissolution of metal results in continuous increase in the rate of corrosion of copper and iron in 1.0 N NaCl + 0.1 N NaOH. In the corrosion of all the metals investigated in an acid medium, not only oxygen depolarization, but also hydrogen depolarization occurs. Iofa and Mikulin [7] showed that with rise in temperature hydrogen overvoltage diminishes and the rate of discharge of hydrogen ions increases.

Frumkin and co-workers [8] showed that, when the slow stage in the corrosion of a metal is the discharge of hydrogen ions, the autosolution current i_c is given by the following equation:

$$i_c = K\,[H^+]^{\frac{\beta}{\alpha+\beta}} e^{-\frac{W_v}{RT}}.$$

It follows that the logarithm of the rate of corrosion is a linear function of $\frac{1}{T}$:

$$\log i_c = A - \frac{B}{T},$$

in which A and B are constants. It follows from Fig. 6 that for the corrosion of iron, copper, nickel, and zinc in an acid medium this relationship is in fact found.

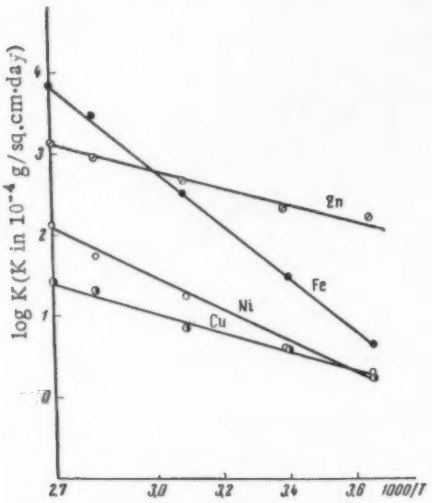
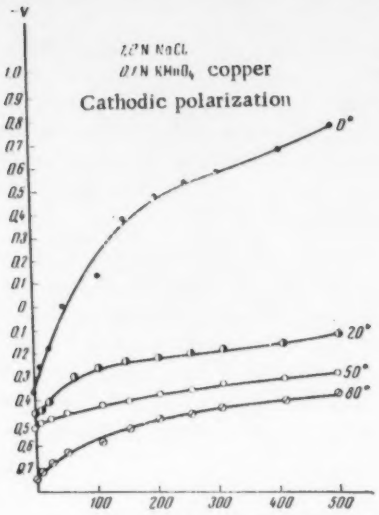


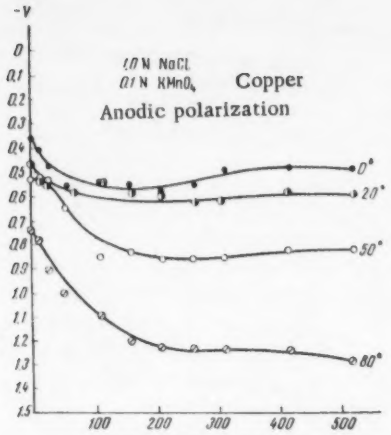
Fig. 6. Effect of temperature on the rate of corrosion of metals in 1.0 N NaCl + 0.1 N HCl.

As our experiments showed, in all media magnesium corrodes with liberation of hydrogen. For this reason its corrosion increases continuously with rise in temperature (Fig. 2). Several workers [9, 10] have shown that the rate of corrosion of magnesium in an acid medium depends on the efficiency of the stirring of the electrolyte. It may be supposed, therefore, that as a result of the high rate at which magnesium corrodes in an acid medium, the controlling factor will be the rate of transport of hydrogen ions to the magnesium surface. A tentative calculation of the limiting diffusion current due to H^+ in 1.0 N NaCl + 0.1 N HCl gives the value I_d = 10 ma/sq. cm. Values of 10^{-4} sq. cm/second for the diffusion coefficient of H^+ and δ = 0.075 cm for the thickness of the diffusion layer were taken from [11]. The density of the corrosion current, calculated from corrosion losses, is 7.5 ma/sq. cm. The results speak in favor of diffusion control. The increase in the rate of diffusion of hydrogen ions with rise in temperature results in increase in the rate of corrosion of magnesium.



Current density (μa/sq.cm)

Fig. 7. Cathodic polarization of copper in 1.0 N NaCl + 0.1 N $KMnO_4$.



Current density (μa/sq.cm)

Fig. 8. Anodic polarization of copper in 1.0 N NaCl + 0.1 N $KMnO_4$.

TABLE

Rates of Corrosion (10^{-4} g/sq.cm per day)

Medium	Temperature (°C)	Rate of corrosion (10^{-4} g/sq. cm·day)					
		Copper	Iron	Nickel	Lead	Magnesium	Zinc
1.0 *N* NaCl	20	0.75	1.33	0	0.97	53 2	1.38
	50	2.96	5.6	0.9	11.3	126.0	9.5
	80	11.3	6.9	1.2	17.8	213.0	19.0
	95	8.25	6.1	1.75	10.3	271.0	9.0
1.0 *N* NaCl	0	3.08	16.0	0.95	1.21	12.2	0.35
	20	5.33	181.0	2.19	3.49	30.6	3.77
0.1 *N* $KMnO_4$	50	8.3	1580.0	43.0	23.5	29.3	471.0
	80	3.53	1783.0	1121.0	278.0	61.0	1651.0
	95	3 0	2450.0	2330 0	450.0	80.0	2460.0
1.0 *N* NaCl	0	1.86	4.45	1.87	5.34	630	171
	20	3.92	31.0	2.85	11.1	810	196
	50	7.0	308.0	16.1	28 3	1290	453
0.1 *N* HCl	80	21.0	3280.0	54.0	39.2	3960	950
	95	25.7	6430 0	131.0	44.3	9000	1350
1.0 *N* NaCl	0	0.7	0.153	—	6.25	11.6	2.17
	20	0.72	1.13	—	9.73	33.0	2.55
	50	4.1	1.74	—	28.5	67.0	12.4
0.1 *N* NaOH	80	7.8	3.15	—	34.0	108.0	30.1
	95	11.6	4.7	—	28.0	120.0	22.0

Temperature coefficient of rate of corrosion (mean) (% per degree)

1.0 *N* NaCl	5.7*	2.9*	3.4	4.5*	3 5	3.6*
1.0 *N* NaCl+ +0.1 *N* $KMnO_4$	2.4*	10.7	13.0	9.3	3.6	11.0
1.0 *N* NaCl+ +0.1 *N* HCl	4.0	10.6	5.4	3.3	3.7	5.1
1.0 *N* NaCl+ +0.1 *N* NaOH	3.9	6.9	—	2.4	3.4	4.1*

*In temperature range 20-80°; remainder in range 0-95°.

Investigations on the kinetics of the electrode processes showed that in a neutral oxidative medium (1.0 N NaCl + 0.1 N $KMnO_4$) iron, nickel, lead, and zinc corrode under cathodic control. Since the concentration of depolarizer (potassium permanganate) does not change with rise in temperature, the rate of corrosion of these metals rises continuously. The rate of corrosion of copper in this medium passes through a maximum with rise in temperature (Fig. 2). According to the experimental results, with rise in temperature cathodic polarization diminishes (Fig. 7) and anodic polarization increases (Fig. 8). At 0° and 20° there is cathodic control, at 50° mixed control, and at 80° and 95° anodic control.

It follows from our electrochemical and corrosion investigations that potassium permanganate plays a dual part in corrosion: on the one hand it is a depolarizer and increases the rate of the cathodic process (thus it follows from the Table that up to 50° the rate of corrosion of copper in neutral oxidative solution is greater than in the other media), and on the other hand it is a passivator [1], and with rise in temperature retards the anodic process in ever-increasing degree. The result of these two opposed effects of permanganate is a complicated relation between rate of corrosion of copper and temperature. It follows from the data in the Table that the greatest rises in the rate of corrosion with rise in temperature, i.e. the highest temperature coefficients of rate of corrosion

$$T_k = \frac{Kt + 1\nu}{Kt},$$

are found in a neutral oxidative medium, in the case of the metals investigated.

SUMMARY

1. An investigation was made into the effect of temperature on the rate of corrosion and kinetics of the electrode processes for copper, iron, nickel, magnesium, and zinc in 1.0 N NaCl, 1.0 N NaCl + + 0.1 N HCl, 1.0 N NaCl + 0.1 N NaOH, and 1.0 N NaCl + 0.1 N $KMnO_4$.

2. Confirmation was found for our previous conclusion [12]: the variation of the rate of a corrosion process with change in temperature is due primarily to change in the factor controlling the given corrosion process.

3. Investigation of the kinetics of the cathodic reduction of oxygen at platinum in 1.0 N NaCl showed that with rise in temperature the overvoltage for ionization of oxygen diminishes, on the average, by 2.8 mv per degree.

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EFFECT OF ADDITIONS OF HYDROCARBONS ON THE CONCENTRATION LIMITS FOR FLAME PROPAGATION IN GAS MIXTURES CONTAINING HYDROGEN

E. A. Blyumberg, V. I. Vasilyev, and N. M. Emanuel

The problem of inhibiting combustion processes in explosive mixtures of inflammable gases with oxygen or air is one of pressing importance in various branches of technology. The most widespread method of preventing explosion is dilution of the mixture with an inert gas (N_2, CO_2, and others) and increase in the concentration of one of the components of the combustible mixture. Both these methods of passivating explosive mixtures have the fundamental defect of rendering them often of little or no value for practical use (the original mixture has to be diluted many times).

In work devoted to explosion hazards in gases and vapors, much attention has been paid to the selection of noninflammable substances whose addition in small amounts results in a substantial restriction of the range of flame propagation in the combustible mixture. As inhibitors of this sort, various halogen-containing compounds are used: fluorine-containing substances have recently come into extensive use. However, in many cases, halogen compounds are unsuitable because of the undesirability of introducing halogen into the system (corrosion and other chemical reaction).

Hence, having set ourselves the task of finding inhibitors for hydrogen-air mixtures, we first turned to a new class of inhibitors which are free from the above defects, namely, to combustible inhibitors and, in particular, to hydrocarbons. The point is that additions of small amounts (of the order of 10-15%) of substances forming explosive mixtures with air to highly explosive mixtures of another combustible substance with air results in complete prevention of flame propagation in the resulting ternary mixture. Apart from its practical importance, this phenomenon is of great scientific interest since it may provide a key to the understanding of the nature of concentration limits.

Several recent papers [1-3] report the inhibiting action of various hydrocarbons on flame propagation in mixtures of hydrogen with oxygen and air.

It was shown [1] that addition of 10% of methane renders the stoichiometric mixture of hydrogen and air safe, though this mixture is extremely explosive in absence of inhibitor. This property of methane has found practical application in the manufacture of hydrogen peroxide from hydrogen and air [2].

In the investigation [3], the effect of toluene, some alcohols, halogen compounds, and isooctane on the upper limit of flame propagation in a hydrogen-air mixture was studied. An interesting phenomenon was observed: small additions of inhibitors (of the order of 1-2%) have a greater effect than large additions. Accordingly, the curve for the dependence of the hydrogen content at the upper limit on the amount of addition has a sharp bend; the section following this bend is a straight line. The authors base their explanation of this relationship on the le Chatelier principle [4]. The inhibiting effect increases as the number of carbon atoms in the molecule of the additive increases.

Comparing the behavior of additives belonging to other classes of organic compounds, several authors [3, 5, 6] have noted diminution in the effectiveness of inhibiting action along the series $(C_2H_5)_3N$, C_2H_5I, C_2H_5Br, C_2H_5OH, $C_2H_5ONO_2$.

Egerton and Powling [7] consider that the inhibiting action of additives is determined mainly by the thermochemistry of the system, but an important part is played also by the chemical factor: suppression of the branched-chain reaction of $H_2 + O_2$ due to reaction of active centers of the chain with the halogen

residue of the inhibitor (CH I, CH Br). Several authors, in studies of the inhibiting action of various additives both in hydrogen-air mixtures [8-10] and in other combustible gas mixtures [11], concluded that the chemical factor was the most important in determining the concentration limits for flame propagation.

Zeldovich [12] concluded, on the basis of a quantiative treatment, that with the introduction of small amounts of halogen compounds as flame-propagation suppressors in explosive mixtures (hydrogen-air mixtures, in particular) the thermal properties of the mixtures changed very little. Calculations showed that addition of carbon tetrachloride has no effect on the combustion temperature, its inhibiting effect being associated with action on the rate of chemical reaction.

EXPERIMENTAL

Procedure. The concentration limits for flame propagation in combustible mixtures containing hydrogen were determined in spherical glass flasks, diameter 8 cm, having sealed-in electrodes of molybdenum wire. Ignition of the mixture was effected by a high-tension spark produced by the discharge of a 2-microfarad condenser. A more detailed description of the method of determining concentration limits is given in a previous paper [13].

As inhibitors for flame propagation we used methane, propane, butane, isobutane, and benzene. Mixtures were prepared in the explosion flask at room temperature and 760 mm pressure.

EXPERIMENTAL RESULTS

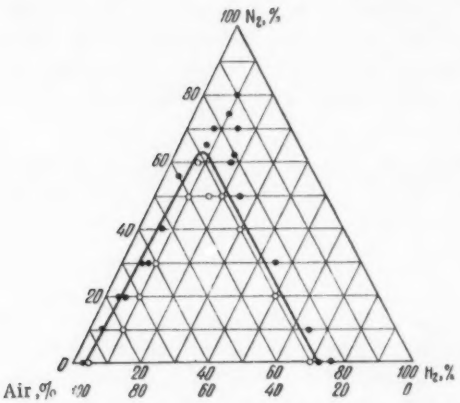

Fig. 1. Flame-propagation region in mixtures of H_2 + air + N_2: ○ - mixture explodes; ● - mixture does not explode (the same denotation is used in Figures 2 - 7)

Flame-propagation Region in Mixtures of H_2 + + Air + N_2 and H_2 + Air + N_2 + CCl_4. Our object was to study the action of combustible inhibitors, but we first determined the concentration limits for flame propagation in hydrogen-air mixtures passivated with nitrogen and carbon tetrachloride so that we could later judge the inhibiting effects of hydrocarbons with the help of a comparison of results. The experimental results obtained in this series of experiments are presented in triangular coordinates in Fig. 1, in which explosive mixtures are denoted by circles and nonexplosive by circular spots. The region of flame propagation is represented by the area bound by the curve drawn between the circles and the spots and by the horizontal axis. As the mixture is diluted with nitrogen, the region of flame propagation narrows, and with the addition of 65% of nitrogen, flame propagation will not occur in the mixture, irrespective of the relative amounts of hydrogen and air.

Addition of 10% of carbon tetrachloride narrows the region of flame propagation and reduces the amount of nitrogen required for the complete passivation of hydrogen-air mixtures from 62% to 42%.

Concentration Limits for Flame Propagation in Hydrogen-Air Mixtures Containing Hydrocarbons. When small amounts of CH_4, C_3H_8, n-C_4H_{10}, i-C_4H_{10}, and C_6H_6 were introduced into hydrogen-air mixtures, a considerable lowering of the upper concentration limit for flame propagation was observed. Figures 2 and 3 represent the relationships that we found between the upper limit (expressed as hydrogen concentration) and the percentage addition of hydrocarbon. The percentage content of air at each point was determined by difference (100% less [% of hydrogen + % of additive]). Fig. 4 (Curve 1) shows the analogous relation for inhibition with carbon tetrachloride. On examination of the curves in Figures 2-4 it will be seen that small additions have the greatest effect; as the addition increases, the lowering of the percentage of hydrogen at the upper limit becomes less.

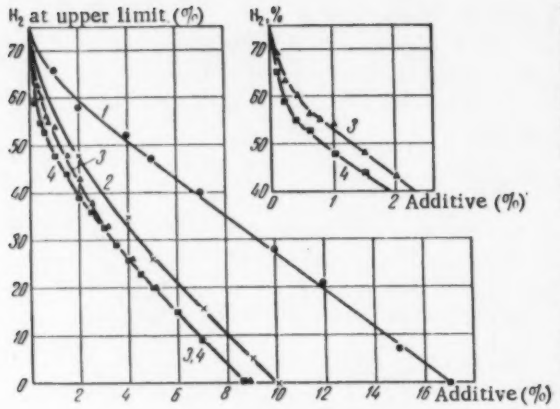

Fig. 2. Dependence of upper concentration limit (hydrogen concentration) for flame propagation in hydrogen-air mixtures on the amount of added hydrocarbon: 1) addition of CH_4; 2) addition of C_3H_8; 3) addition of n-C_4H_{10}; 4) addition of i-C_4H_{10} (the upper graph shows the initial portions of Curves 3 and 4).

The difference that we have established in this investigation between the inhibiting effects of n-C_4H_{10} and i-C_4H_{10} is of special importance. These two isomers have almost identical thermal properties, but the upper limit for a hydrogen-air mixture is lowered to a much greater extent by additions of i-C_4H_{10} than by additions of n-C_4H_{10}. Thus, for additions of 0.2%, n-C_4H_{10} lowers the upper limit to 66%, whereas i-C_4H_{10} lowers it to 56% of hydrogen.

It is interesting and, at first glance, incomprehensible that the addition to a hydrogen-air mixture of an amount of hydrocarbon equal to (or greater than) the concentration limit for flame propagation in a mixture of the given hydrocarbon and air [14] results in the complete passivation of the hydrogen-air mixture. Thus, in mixtures containing more than 17% of CH_4, 10% of C_3H_8, 9% of n-C_4H_{10} or i-C_4H_{10} (Fig. 2), and 8% of C_6H_6 (Fig. 3), flame is not propagated, whatever the relative amounts of hydrogen and air may be. It is noteworthy that the inhibiting effect of hydrocarbons increases as the number of carbon atoms in the hydrocarbon molecule increases.

Concentration Limits for Flame Propagation in $H_2 + Cl_2$ and $H_2 + NO$ Mixtures having Additions of Propane. It was considered to be of importance to establish whether the inhibiting effect of hydrocarbons is peculiar to hydrogen-air (or -oxygen) mixtures or extends to other combustible mixtures containing hydrogen.

As an example we took the action of propane on the concentration limits for flame propagation in $H_2 + Cl_2$ and $H_2 + NO$ mixtures. The results of this series of experiments are presented in Fig. 5. The upper limit that we found for flame propagation in a hydrogen-chlorine mixture at atmospheric pressure with spark ignition (86% of H_2) was the same as that reported in the literature [15]. Addition of propane resulted in lowering of the upper limit. We obtained a similar result for the inhibiting action of propane on a mix-

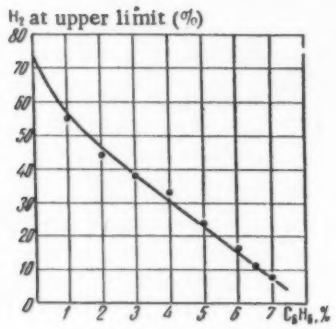

Fig. 3. Dependence of upper concentration limit (hydrogen concentration) for flame propagation in hydrogen-air mixtures on the amount of added benzene.

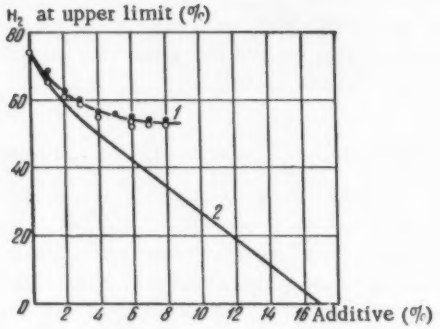

Fig. 4. Comparison of the inhibiting actions of CH_4 and CCl_4 on flame propagation in hydrogen-air mixtures: 1) addition of CCl_4; 2) addition of CH_4 (transcribed from Fig. 2).

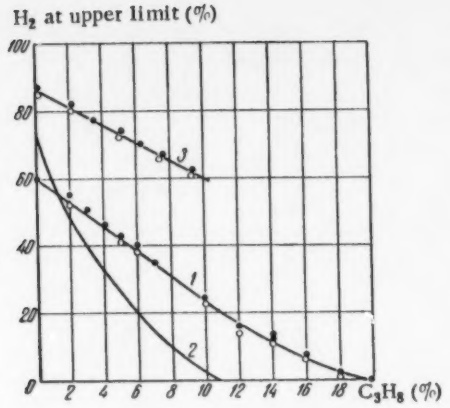

Fig. 5. Dependence of upper concentration limit for flame propagation in H_2 + NO (Curve 1) and H_2 + Cl_2 (Curve 3) mixtures on the amount of added propane. Curve 2 is the analogous relationship for hydrogen-air mixtures (transcribed from Fig. 2).

ture of hydrogen and nitric oxide. The concentration limits for flame propagation in H_2 + NO mixtures were determined by us recently [13] (upper limit 60% of H_2, lower limit 11.4% of H_2). Comparison of the curves in Fig. 5 shows that the inhibiting effect of propane on H_2 + Cl_2 and H_2 + NO mixtures is similar to but somewhat weaker than its effect on hydrogen-air mixtures.

Concentration Limits for Flame Propagation in Mixtures of Hydrocarbons with Air, Hydrogen, and Nitrogen. The difference in the inhibiting effects of n-C_4H_{10} and i-C_4H_{10} is shown particularly clearly when the amount of hydrocarbon added is small. For additions greater than 1%, the difference is less, and for additions of 3% or more, there is no difference in their effect ; the upper limits for flame propagation are identical (Fig. 2, Curves 3 and 4). It would naturally be expected that the reduction in the effectiveness of additions as the amount of hydrocarbon introduced increases would be associated, as usual in chain reactions, with the fact that the amount added is sufficient for considerable chain termination to occur. This is the picture that we actually observed in our experiment in the case of the inhibiting action of carbon tetrachloride. It will be seen from Fig. 4 that increase in the amount of carbon tetrachloride in a hydrogen-air mixture beyond 5% has almost no effect on the upper limit. In the case of combust-

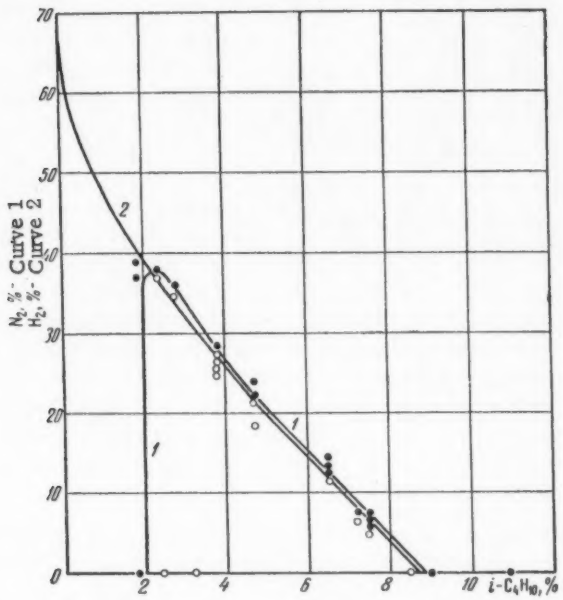

Fig. 6. Dependence of the amount of nitrogen at which flame propagation ceases in a mixture of i-C_4H_{10} and air on the concentration of i-C_4H_{10} (Curve 1). Curve 2) dependence of upper limit (as H_2 concentration) in hydrogen-air mixtures on amount of i-C_4H_{10} added (transcribed from Fig.2).

TABLE

Composition of Mixture at Which Flame Propagation in Mixture Ceases

Content (%) of				Content (%) of			
hydrocarbon	air	hydrogen	nitrogen*	hydrocarbon	air	hydrogen	nitrogen*
5.0 CH_4	76.0	19.0	—	5.0 n-C_4H_{10}	75.0	—	20.0
5.0 CH_4	73.0	—	22.0	5.0 C_6H_6	78.0	17.0	—
5.0 C_3H_8	67.0	28.0	—	5.0 C_6H_6	77.0	—	18.0
5.0 C_3H_8	65.0	—	30.0	10.0 CH_4	63.0	27.0	—
5.0 n-C_4H_{10}	77.0	18.0	—	10.0 CH_4	65.0	—	25.0

* Amount of added nitrogen, no account being taken of atmospheric nitrogen.

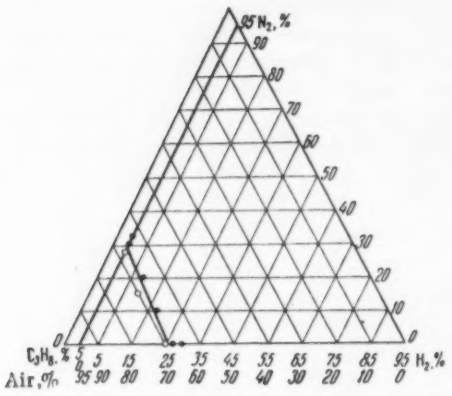

Fig. 7. Flame-propagation region for C_3H_8 + air + $+H_2$ + N_2 mixtures at constant C_3H_8 concentration (5%).

ible inhibitors, however, no such plateau is observed on the curve for the relation of the upper limit to the concentration of inhibitor. The curves in Fig. 2 have only a small bend, beyond which there is a linear section. We supposed, however, that in this case also there is a certain limiting concentration of inhibitor, sufficient to suppress the chain reaction. For example, for butane and isobutane this limiting concentration is attained when 3% has been added, which corresponds to the concentration at which the difference in inhibiting effect of n-C_4H_{10} and i-C_4H_{10} disappears. We supposed further that mixtures having a higher hydrocarbon content than this "limiting concentration" would no longer behave like hydrogen-air mixtures, but like mixtures containing only one combustible substance, the hydrocarbon, and also that hydrogen would play the part of inert diluent. In order to check this supposition we carried out special experiments on the inhibiting effect of nitrogen on the concentration limits for flame propagation in hydrocarbon-air mixtures. The results of experiments on isobutane are presented in Fig. 6 (Curve 1) in the form of the relation of the percentage of nitrogen completely passivating the mixture to the content of combustible (i-C_4H_{10}) in the mixture. For comparison purposes, the relation of the upper limit (% H_2) on amount of i-C_4H_{10} added is also given in Fig. 6 (Curve 2). The coincidence of Curves 1 and 2 shows that at all i-C_4H_{10} concentrations above 2.5% the amounts of nitrogen and hydrogen necessary for nonpropagation of flame in isobutane-air mixtures are identical.

This result supports our suggestion that in inhibited mixtures hydrogen plays the part of inert diluent with respect to an isobutane-air mixture (see Table).

Further experiments for air mixtures containing 10% of CH_4, 5% of C_3H_6, 5% of n-C_4H_{10}, or 5% of C_6H_6 showed that this result is not peculiar to isobutane, but is closely reproduced in all the systems that we have studied. We determined the regions of flame propagation for dilution of these mixtures with various amounts of nitrogen and hydrogen and showed that all the mixtures are passivated by the same amount of inert gas, whether this be nitrogen, hydrogen, or a mixture of nitrogen and hydrogen. Let us take, for example, the mixture containing 5% of C_3H_8 (Fig. 7). Flame propagation in this mixture ceases when part of the air is replaced by nitrogen or hydrogen, the amount required being 30% of N_2, 20% of N_2 + 10% of H_2, 10% of N_2 + 18% of H_2, or 17% of H_2.

DISCUSSION OF RESULTS

From the results of this investigation we may conclude that the great differences in the inhibiting effects of hydrocarbons and other additives are associated mainly with their chemical effects and not with changes in the thermal properties of the system. This follows from the high effectiveness of small additions of inhibitors, from the great difference in the action of CH_4 and CCl_4, which are similar in heat capacity, and particularly from the difference in effectiveness between isobutane and butane, which have almost identical thermal characteristics. This conclusion is in accord with the conclusion, reached in the investigations [8-12], concerning the determining part played by the chemical factor in the value of the concentration limits for flame propagation in a combustible mixture.

In studying the nature of this chemical action, we started from the analogy between reactions initiated by a spark and the corresponding reactions at lower temperatures, because at present we do not have sufficient reliable data on the kinetics and chemistry of reactions in flames. The permissibility of such a comparative method in our case is confirmed by the close resemblance of the inhibiting effect of hydrocarbons on flame propagation in spark-ignited mixtures to the action of additions of hydrocarbons on the limits of chain autoignition of mixtures of hydrogen with oxygen.

The change in effectiveness of inhibiting action as we pass from one hydrocarbon to another is probably to be associated with the difference in reactivity between one inhibitor and another with respect to the atoms and radicals present in the system.

This view receives particular support from a comparison of the experiments with additions of CH_4 and CCl_4 (Fig. 4). As will be seen from Fig. 4, additions of CH_4 lowers the upper limit for flame propagation in hydrogen-air mixtures to a greater extent than equal additions of CCl_4. If, however, we supposed that the inhibiting effect of additions is associated with removal of H atoms from the sphere of reaction by reaction with an inhibitor molecule or radical, then the effect should be the reverse. According to modern concepts of the reactivity of molecules and radicals, as generalized in Semenov's book [16], reaction of H atoms with CCl_4 requires a lower expenditure of energy than reaction of H with CH_4, since the energy of rupture of the C — Cl bond in CCl_4 (68.4 kcal) is less than the energy of rupture of the first C— H bond in CH_4 (101 kcal). On the basis of these considerations it must be concluded that inhibition by methane proceeds not only through its reaction with H atoms, but also as a result of its reaction with other radicals present in the system. Of such radicals, OH must receive particular consideration, for the presence of large amounts of OH radicals in a reacting $H_2 + O_2$ mixture was established experimentally in the investigations of Kondratyev [17] and Avramenko [18].

The view that OH radicals play a substantial part in the mechanism of inhibition by hydrocarbons is supported also by experiments on the concentration limits for flame propagation in hydrogen-chlorine mixtures containing propane. In the combustion of a hydrogen-chlorine mixture, OH radicals are known to be absent, and the inhibiting action of hydrocarbons is here limited by the possibility of reaction between the inhibitor and H atoms.

Hence, if our suggestion is correct, propane should have a greater effect on hydrogen-air mixtures than on hydrogen-chlorine mixtures. Exactly this relationship was observed for the effectiveness of propane in our experiments (Fig. 5). It must be pointed out, however, that the results of our comparison of the combustion of hydrogen-air and hydrogen-chlorine mixtures are only approximate in character, since we are here dealing with reactions proceeding by essentially different mechanisms.

Our conclusions to the effect that the restriction of the regions of flame propagation in hydrogen-air mixtures is associated with reaction of hydrocarbon molecules with active centers of the chain reaction (H, OH) are in accord with results obtained in work on the chain autoignition of hydrogen-oxygen mixtures.

The phenomenon of the displacement of autoignition limits of hydrogen-oxygen mixtures by additions of hydrocarbons has been known for a fairly long time, and several investigations have been devoted to this matter. Voevodsky and Tikhomirova [19] made a detailed investigation of the displacement of the second limit in presence of ethane, propane, ethylene, isobutane, and propene. On the assumption, based on quantitative measurements, that the concentration of H atoms in a hydrogen-oxygen flame is about ten times as great as the concentration of other atoms and radicals, the authors consider that displacement of

the limits is associated mainly with the reaction $RH + H \rightarrow R + H_2$ (RH is a hydrocarbon molecule), and they use their data on the displacement of limits in the quantitative determination of the rate constant of this reaction.

Baldwin and co-workers also consider that the displacement of the second limit of the chain autoignition of a hydrogen-oxygen mixture, which they observed for additions of ethane [20] and propane [21], is due to reaction of hydrocarbon molecules with H atoms. According to the inhibition mechanism proposed by these authors, the hydrocarbon radicals formed react with an oxygen molecule with formation of HO_2 radicals of low activity, which are unable to continue the chain. In a later review article [22] the reaction of $C_2H_6 + OH$ is also taken into account, but it plays a less important part than the reaction of $C_2H_6 + H$ and becomes important only at low H_2 concentrations.

Levy [23] explains the lowering of the second flame limit of a hydrogen-oxygen mixture by additions of CH_4 and C_3H_8 by reaction of the additive with H, O, and OH, and also by the strong inhibiting action of formaldehyde, formed by oxidation of the added hydrocarbon.

Hence, in most papers on the action of hydrocarbons on the chain autoignition of hydrogen-oxygen mixtures the main role in the inhibition process is ascribed to the reaction of hydrocarbon with H atoms, whereas under the conditions of the present investigation, not only this reaction, but also, probably, reaction with participation of OH radicals is of considerable significance.

These considerations apply mainly to the first part of the process, i.e., to the suppression of the branched chain reaction of oxidation of hydrogen by the addition of hydrocarbons.

What then are the causes of the phenomena that we observed for high additions of hydrocarbons, i.e., under conditions in which we consider the branched chain reaction of oxidation of hydrogen to be almost completely suppressed? It is probable that the important determining factor here lies in the fact that the rate of the degenerate branched process of oxidation of the hydrocarbon is greater than that of the oxidation of hydrogen, and all the oxygen is used in oxidation of the hydrocarbon until the point is reached at which the oxidation of hydrogen becomes of importance. Hydrogen, therefore, acts as an inert gas with respect to the combustible hydrocarbon-air mixture.

This hypothesis is in accord with results obtained in the slow oxidation of hydrogen (560°, 420 mm) in presence of propane [24]. In this case additions of propane result in extension of the region of autoignition (as compared with hydrogen-oxygen mixtures in absence of propane). At the start of reaction there is a rapid increase in pressure (due to oxidation of propane) which is accompanied after a short time by ignition of the hydrogen. The minimum concentration of propane bringing about this induced ignition depends on the O_2 concentration, but is independent of H_2 concentration, which again indicates independent successive oxidation of propane and hydrogen.

The pressure rise in the second stage, which characterizes the extent of oxidation of hydrogen, greatly depends on the H_2 and C_3H_8 concentrations. A deficiency of oxygen below that required for the complete combustion of propane and hydrogen has no effect on the stage of propane oxidation, whereas the second stage proceeds only to an extent corresponding to the amount of oxygen that did not react in the first stage.

A similar picture would appear to be observed in our experiments. On the basis of these ideas it becomes clear why complete passivation of hydrogen-air mixtures is attained in all cases at hydrocarbon concentrations equal to the upper limit for flame propagation in a mixture of the given hydrocarbon with air. In these cases we seem to be dealing not with a complicated mixture of two combustible substances and air, but with a hydrocarbon-air mixture passivated with hydrogen. It is obvious that flame propagation will cease in such a mixture at hydrocarbon concentrations above the upper concentration limit.

SUMMARY

1. The concentration limits were determined for flame propagation in hydrogen-air mixtures having additions of methane, propane, butane, isobutane, and benzene, in $H_2 + Cl_2$ and $H_2 + NO$ mixtures in presence of propane, and in mixtures, diluted with hydrogen and nitrogen, of methane, propane, butane, and benzene with air.

2. It was concluded that the addition of small amounts of hydrocarbons to hydrogen-air mixtures results in lowering of the upper limit for flame propagation owing to chemical reaction between the inhibitor and active centers in the oxidation of hydrogen. As the amount of the addition is increased, the chain reaction of hydrogen with oxygen is suppressed to such an extent that combustion of the added hydrocarbon begins to play a determining role (hydrogen then plays the part of inert diluent).

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SYNTHESIS OF ARYLPYRAZOLES

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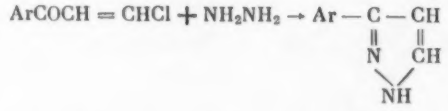
Some years ago we developed a new, convenient method for the synthesis of alkylpyrazoles by the condensation of alkyl 2-chlorovinyl ketones with hydrazine and arylhydrazines [1]. Thanks to our recent development of a method of synthesizing aryl 2-chlorovinyl ketones [2], these substances have now become as accessible as their aliphatic analogs. As a result it is possible to extend various syntheses based on alkyl 2-chlorovinyl ketones to the preparation of analogous products of the aromatic series.

The present paper is devoted to the application of aryl 2-chlorovinyl ketones to the synthesis of 3--aryl- and 1,3-diaryl-pyrazoles, which are, as yet, relatively little known compounds, the only sufficiently general method of synthesizing them being the condensation of hydrazines with benzoylacetaldehydes.

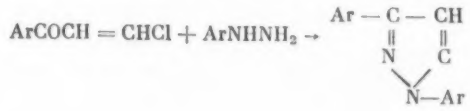
Study of reaction between aryl 2-chlorovinyl ketones and hydrazine showed that it is able to yield a great variety of 3-arylpyrazoles:



$Ar = C_6H_5,\ p\text{-}NO_2C_6H_4,\ m\text{-}NO_2C_6H_4,\ p\text{-}ClC_6H_4,\ o\text{-}ClC_6H_4,\ o\text{-}BrC_6H_4$

In comparison with the synthesis of alkylpyrazoles [1], the reaction requires somewhat more severe conditions: it is generally carried out by heating an equimolecular mixture of the reactants in ether or acetic acid. Arylpyrazoles are obtained in high yields (70-90%) and are readily isolated in the pure state by the usual methods. In this way we prepared 3-phenyl-, 3-p-chlorophenyl-, 3-o-chlorophenyl-, 3-o--bromophenyl-, 3-p-nitrophenyl-, and 3-m-nitrophenyl-pyrazoles, most of which have not been described in the literature. The aryl 2-chlorovinyl ketones required for the synthesis were prepared by the general method that we developed recently [2], and two of them, 2', 3-dichloroacrylophenone and 3-chloro-3'--nitroacrylophenone, were prepared for the first time. Our proposed method for the synthesis of 3-arylpyrazoles is therefore sufficiently general in character and is distinguished by the simplicity and convenience with which it is carried out, the accessibility of the starting materials, and the high yields obtained.

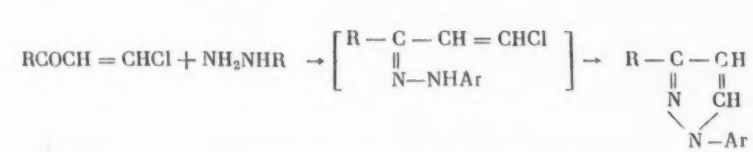
We studied also the condensation of aryl 2-chlorovinyl ketones with arylhydrazines (phenyl- and p-nitrophenyl-hydrazines). It was found that this reaction proceeds just as smoothly as the first one and, what is particularly important, leads to the formation of pure 1,3-diarylpyrazoles:



In this connection we must point out that the condensation of benzoylacetaldehydes with arylhydrazines, previously the only general method for the synthesis of 1,3-diarylpyrazoles [5], often proceeds in two directions with formation of a mixture of 1,3- and 1,5-diarylpyrazoles. Thus, the question of the structure of the diarylpyrazoles obtained by the condensation of benzoylacetaldehydes with phenylhydrazine was the subject of prolonged discussion [6]. Hence, the synthesis of diarylpyrazoles by this method must generally be followed by verification of the structure of the product. In our case, i.e., in the condensation of aryl--2-chlorovinyl ketones with arylhydrazines, we always obtained only one compound, the constants of which always corresponded to those of the 1,3 isomer when the latter were known from the literature. Even without purification the product had a melting point extremely close to that of the 1,3-diarylpyrazole; none of the other possible isomer, the 1,5-diarylpyrazole, was found. It is clear that if the latter is formed, then it is formed in such small amounts that for practical purposes the reaction can be regarded as quite unequivocal in direction, which cannot be said of the reaction of benzoylacetaldehydes with arylhydrazines. It is this fact, together with the accessibility of the starting materials, which distinguishes our method from the known method and enables us to regard it as the most convenient preparative synthesis of 1,3-diarylpyrazoles.

It must be pointed out that the condensation of aryl 2-chlorovinyl ketones with arylhydrazines requires more severe conditions than the analogous reaction of alkyl 2-chlorovinyl ketones: it is necessary to heat the mixture of reactants in acetic acid or alcohol, and the process must sometimes be continued for up to ten hours. This indicates the somewhat lower reactivity of aryl 2-chlorovinyl ketones in comparison with their aliphatic analogs, which we have already noted in connection with the synthesis of flavylium salts [7].

The unequivocal course of the reaction of aryl 2-chlorovinyl ketones with arylhydrazines can be explained, of course, only by the formation of the arylhydrazone of the aryl 2-chlorovinyl ketone in the first stage of the reaction and by the further cyclization of this with elimination of hydrogen chloride and formation of the corresponding pyrazole derivative:



We have previously made a similar suggestion regarding the mechanism of the reaction [1]; we may now present experimental proof of the correctness of this view. It was found that in reaction with p-nitrophenylhydrazone under mild conditions at room temperature 4-chloro-3-buten-2-one rapidly forms its p--nitrophenylhydrazone. This substance, merely by being heated in boiling acetic acid for 1-2 minutes, is quantitatively cyclized to 3-methyl-1-p-nitrophenylpyrazole. The same cyclization can be brought about by fusion of the p-nitrophenylhydrazone, which melts at 120-121° with frothing (liberation of hydrogen chloride.) to a melt that rapidly solidifies and gives a substance of m.p. 163-165°, which corresponds to the pyrazole derivative. This hydrazone is affected even by recrystallization, and it is doubtless for this reason that it was erroneously described by Petrov and Sopov [8] as a substance of m.p. 142° which the authors could not obtain in an analytically pure state.

These results show without doubt that the first stage of the reaction of aryl 2-chlorovinyl ketones with hydrazines is the formation of a hydrazone, which is then cyclized into a pyrazole derivative. As a consequence, reaction proceeds in one direction only.

EXPERIMENTAL

2',3-Dichloroacrylophenone. This was prepared, similarly to 3,4'-dichloroacrylophenone [2]; from 22.5 g of o-chlorobenzoyl chloride and 16.5 g of anhydrous aluminum chloride in 70 ml of dry dichloroethane (the complex was prepared at 3-7°; acetylene was passed for 6-6.5 hours at 40-46°). The yield of 2',3-dichloroacrylophenone was 16.5 g (65%); b.p. 145-146° (15 mm); m.p. 41-43°.

Found %: C 53.63, 53.47; H 3.10, 3.07; Cl 34.92, 35.0. $C_9H_6Cl_2O$.

Calculated %: C 53.71; H 3.01; Cl 35.27.

The substance formed colorless crystals, readily soluble in ether, not so soluble in petroleum ether, and insoluble in water.

3-Chloro-3'-nitroacrylophenone. This was prepared, similarly to 3-chloro-4'-nitroacrylophenone [2], from 2.7 g of m-nitrobenzoyl chloride and 20.0 g of aluminum chloride in 70 ml of dichloroethane. Acetylene was passed for four hours at 45-50°. Yield 8.0 g (31%); m.p. 72°.

Found %: C 51.50; H 2.91. $C_9H_7N_3O_2$.

Calculated %: C 51.08; H 2.86.

3-Chloro-3'-nitroacrylophenone was obtained as white crystals, readily soluble in the usual organic solvents, not so soluble in petroleum ether, insoluble in water.

3-Phenylpyrazole. Hydrazine hydrate (15.0 g) was gradually added to a vigorously stirred solution of 36.0 g of 3-chloroacrylophenone in 150 ml of glacial acetic acid. Much heat was evolved, and it was necessary to apply cooling. When the vigorous reaction ceased, the mixture was boiled for three hours and then left for one day at room temperature. It was poured into twice its volume of 20% sodium hydroxide solution, and the oil that separated was extracted with ether; ether was evaporated off. The product melted at 73°. Recrystallization from petroleum ether gave colorless crystals, m.p. 76.5-77°; yield 26.3 g (84%). The picrate, prepared in alcohol and crystallized from alcohol, had m.p. 168°. The literature [9] gives m.p. 78° for 3-phenylpyrazole and m.p. 168° for its picrate.

3-o-Bromophenylpyrazole. Hydrazine hydrate (0.28 g) was added to a solution of 1.0 g of 2'-bromo--3-chloroacrylophenone in 25 ml of acetic acid. The mixture was heated to boiling and set aside for one day. It was then poured into water and again left for one day, after which it was extracted with ether; ether was evaporated off. The product, m.p. 125-126°, was obtained in a yield of 0.7 g (71%). Recrystallization from petroleum ether gave needles, m.p. 127°.

Found %: C 48.35, 48.55; H 3.23, 3.27. $C_9H_7N_2Br$.

Calculated %: C 48.45; H 3.17.

3-o-Bromophenylpyrazole is soluble in alcohol and ligroin, less soluble in petroleum ether, and insoluble in water.

3-p-Chlorophenylpyrazole. Hydrazine hydrate (0.33 g) was added to a solution of 1.0 g of 3,4'-dichloroacrylophenone in 25 ml of ether. The mixture was boiled for 1.5-2 hours, cooled, and filtered; ether was evaporated off. After two recrystallizations from water the residue formed colorless crystals, m.p. 98°; yield 0.74 g (79%).

Found %: C 60.56, 60.55; H 3.92, 4.10. $C_9H_7N_2Cl$.

Calculated %: C 60.52; H 3.92.

3-p-Chlorophenylpyrazole is soluble in alcohol, dilute acetic acid, and ligroin; it is not very soluble in water.

3-o-Chlorophenylpyrazole. Hydrazine hydrate (0.33 g) was added to a solution of 1.0 g of 2'3-dichloroacrylophenone in 25 ml of ether. The mixture was boiled for three hours. The precipitate formed was filtered off (m.p. 89-90°), ether was evaporated, and some more of the substance of m.p. 89-90° was obtained. Total yield 0.86 g (97%). Recrystallization from water gave colorless crystals, m.p. 89-90°.

Found %: C 60.62, 60.75; H 4.15, 4.05. $C_9H_7N_2Cl$.

Calculated %: C 60.52; H 3.92.

3-p-Nitrophenylpyrazole. Hydrazine hydrate (0.27 g) was added to a solution of 0.95 g of 3-chloro--4'-nitroacrylophenone in 30 ml of ether. A vigorous reaction set in. The mixture was set aside for one day, and the yellow crystals that separated were then filtered off (m.p. 189-190°). Evaporation of the mother liquor gave a further portion of substance having the same melting point. The total yield was 0.75 g (85%). Recrystallization from dilute acetic acid gave light yellow needles, m.p. 192°. The literature [10] gives m.p. 192°.

3-m-Nitrophenylpyrazole. This was prepared from 0.15 g of hydrazine hydrate and 0.5 g of 3-chloro--3'-nitroacrylophenone in 30 ml of ether. The reaction mixture was left overnight, boiled for one hour, and again left overnight. It was filtered, and ether was evaporated off. The residue, amounting to 0.4 g (93%), melted at 110°. Recrystallization from ligroin gave pale yellow crystals, m.p. 120°.

Found %: C 57.27; H 3.85. $C_9H_7N_3O_2$.

Calculated %: C 57.14; H 3.70.

3-m-Nitrophenylpyrazole is soluble in acetic acid and not very soluble in alcohol and dilute acetic acid.

1,3-Diphenylpyrazole. Phenylhydrazine hydrochloride (1.0 g) was added to a solution of 1.0 g of 3--chloroacrylophenone and 10.0 g of sodium acetate in 25 ml of acetic acid. The mixture was boiled for one hour, left for one day, and then poured into an equal volume of water. The precipitate was filtered off, and recrystallization from ligroin then gave 0.75 g (57%) of yellowish crystals, m.p. 83-84.5°. The literature [11] gives m.p. 84-85°.

3-p-Nitrophenyl-1-phenylpyrazole. In a similar way, reaction between 0.49 g of phenylhydrazine hydrochloride and 0.56 g of 3-chloro-4'-nitroacrylophenone in 15 ml of glacial acetic acid gave, after two crystallizations from ligroin, 0.45 g (64%) of a substance of m.p. 136°.

Found %: C 68.24, 68.29; H 4.37, 4.34. $C_{15}H_{11}N_3O_2$.

Calculated %: C 67.92; H 4.19.

3-p-Nitrophenyl-1-phenylpyrazole forms orange needles, soluble in alcohol, less soluble in ligroin, and insoluble in dilute acetic acid.

3-p-Chlorophenyl-1-phenylpyrazole. Phenylhydrazine hydrochloride (0.95 g) was added gradually to a solution of 1.0 g of 3,4'-dichloroacrylophenone in 20 ml of glacial acetic acid. The mixture was boiled for 8-10 hours and cooled. The precipitated crystals, m.p. 118°, were filtered off. Recrystallization from alcohol gave 0.95 g (75%) of colorless crystals, m.p. 118°. The literature [5] gives m.p. 118°.

1-p-Nitrophenyl-3-phenylpyrazole. p-Nitrophenylhydrazine (0.2 g) was added to a solution of 0.2 g of 3-chloroacrylophenone in 20 ml of absolute alcohol. The mixture was boiled and set aside for one day. The precipitated dark red needles were filtered off. The mother liquor gave more crystals, m.p. 168°. Recrystallization from alcohol gave yellow needles, m.p. 169°; total yield 0.2 g (63%). The literature [12] gives m.p. 169-169.5°.

p-Nitrophenylhydrazone of 4-Chloro-3-buten-2-one. 4-Chloro-3-buten-2-one (0.5 g) was added gradually to a solution of 0.5 g of p-nitrophenylhydrazine in 15 ml of acetic acid at room temperature. There was an immediate precipitate of the p-nitrophenylhydrazone. After one day this was filtered off, washed with 15% acetic acid and with water, and vacuum-dried over phosphoric oxide. The substance formed orange crystals, m.p. 119-120°.

Found %: N 17.88, 17.91. $C_{10}H_{10}N_3Cl$.

Calculated %: N 17.56.

Cyclization of the p-Nitrophenylhydrazone of 4-Chloro-3-buten-2-one. The p-nitrophenylhydrazone (0.2 g) was heated in 10 ml of glacial acetic acid for ten minutes. The solution was cooled and diluted with three times its volume of water. The precipitate was filtered off (yield 0.15 g; m.p. 161-163°). Recrystallization from alcohol gave gleaming brown needles, m.p. 165°, undepressed by admixture of 3-methyl-1-p-nitrophenylpyrazole.

SUMMARY

1. A method was developed for the synthesis of arylpyrazoles by reaction of aryl 2-chlorovinyl ketones with hydrazine and substituted hydrazines (yields: 60-90%).

2. It was shown that aryl 2-chlorovinyl ketones react with substituted hydrazines in one way only with formation of 1,3-substituted pyrazoles.

3. It was shown that the p-nitrophenylhydrazone of 4-chloro-3-buten-2-one is very readily cyclized to a pyrazole derivative, which confirms the view that the condensation of aryl 2-chlorovinyl ketones with substituted hydrazines passes through the stage of hydrazone formation.

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DIRECT REPLACEMENT OF HYDROGEN IN ORGANIC COMPOUNDS BY THALLIUM (THALLATION)

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(Paper read at a General Meeting of the Division of Chemical Sciences of the Academy of Sciences of the USSR, May 25, 1957, and at the Sixteenth International Congress on Pure and Applied Chemistry, June 20, 1957, in Paris)

The direct replacement of hydrogen in organic compounds by a metal or nonmetal is a type of reaction which has found extensive development in the classical reactions of sulfonation, nitration, etc., and also in the preparation of organic compounds of alkali metals [1]. Except in the case of mercury, much less study has been devoted to substitution of this sort brought about by the action of metal salts. Mercuration has received many applications, and it has provided one of the main methods of preparing organomercury compounds [2]. Auration, discovered by Kharasch in 1931 [3], has formed the basis for the preparation of various compounds of the type $ArAuCl_2$ by the action of gold salts on organic compounds. As regards the direct introduction of thallium, Gilman and Abbott, who discovered the reaction in 1943 [4], confined themselves to the single example of the thallation of dibenzofuran and have not returned to this reaction in the fifteen years that have elapsed since their discovery.

In the thallation of dibenzofuran Gilman and Abbott obtained bis-4-dibenzofuranylthallium chloride (Ar_2TlX type). The reaction was carried out in concentrated aqueous solution at 165° for four hours. The low yield (9%) and severe reaction conditions, which possibly distorted the primary result of the process owing to the occurrence of disproportionation, were not favorable to the development of this method.

We were prompted to seek other ways of bringing about thallation, and these led us to different and more successful results [5]. We made use of the readily accessible organic salts of tervalent thallium, and this enabled us, first, to carry out the reaction under very much milder conditions and, second, to obtain organothallium compounds of higher stability.

We carried out the thallation under the following conditions. The organic salt of tervalent thallium (we generally used thallium triisobutyrate [5], which crystallizes well and is readily soluble in organic solvents) was mixed with excess of the organic substance in absence of solvent and heated, generally to 100-110°, for 45-60 minutes. Completion of reaction was recognized by the action of a drop of water on a test sample: organic salts of tervalent thallium are readily hydrolyzed (brown precipitate), but the organothallium compound $ArTl(OOCR)_2$ gives no such coloration. After the usual treatment with petroleum ether (alone or in admixture with diethyl ether), which removes the excess of unchanged organic compound, the organothallium compound was crystallized out. It is important to note that, unlike Gilman [4], and in spite of the use of an excess of the organic compound, in all cases we obtained compounds of the type $ArTlX_2$, and not Ar_2TlX. Our results are presented in the Table.

The Table shows, for example, that the thallation of benzene is slow but gives an excellent yield. The thallation of naphthalene and phenetole does not go so well. Thallium triisobutyrate reacts extremely rapidly (5 minutes) with thiophene. It is interesting, however, that in the thallation of thiophene, even after long heating, we could not detect the entry of more than one $Tl(OOCR)_2$ group (compare mercuration). We could not detect the occurrence of polythallation in any of the other cases, with the exception of that of acetophenone. As regards orientation, the reaction has much in common with mercuration in respect to orienting groups of the first kind (see Table). In thallation thiophene reacts, as usual, in the 2-position; the entry of thallium in the 2-position of naphthalene is somewhat unexpected.

TABLE

Compounds of the Type $ArTlX_2$ (X is isobutyroxy) Obtained by Thallation

Thallated compound	Duration of reaction	Reaction temperature (°C)	Yield (%)	m. p. (°C)	Orientation
Benzene	18 hrs.	100	90	221	-
Toluene	1 hr.	110	55	-	Mixture of isomers
Naphthalene	1 hr.	115	25	209	2-Position
Anisole	30-40 min.	100	44	195	p-Position
Phenetole	1 hr.	100	25	186.5	p-Position
o-Dimethoxybenzene	45 min.	100	75	186-187	4-Position
m-Dimethoxybenzene	45 min.	100	73	147-148	-
p-Dimethoxybenzene	1 hr., 45 min.	95-105	54	112-113	Positions equivalent
1,3,5-Trimethoxybenzene	30 min.	100	87	117-118	Positions equivalent
Thiophene	5 min.	100	88	215-216	2-Position
Acetophenone	5 min.	100	45	127-128	2,2-Disubstitution
Dibenzofuran	2 hrs.	110	50	206-207	2-Position

Thallation can be considered to be an electrophilic-substitution reaction; it proceeds as follows:

$$ArH + Tl(OOCR)_3 \rightarrow ArTl(OOCR)_2 + RCOOH.$$

For the further characterization of the reaction mechanism we require more data on compounds containing m-orienting groups. It may be noted that in these cases reaction proceeds much less readily.

In order to prove the entry of thallium in one or another position we converted the organothallium compounds into the corresponding organomercury compounds (by Challenger's method [6]). Also, rupture of the thallium-carbon bond by the action of iodine or bromine enabled us to prepare and identify the corresponding halogen compounds.

Diisobutyrates of the type $ArTlX_2$ are white crystalline substances, stable to atmospheric moisture (unlike $Tl(OOCR)_3$), sometimes of fairly high melting point (see Table), and soluble in most organic solvents, though least of all in diethyl ether and petroleum ether. Thallation in this way and a reaction of diarylmercury compounds that we have discovered* provide new methods for the preparation of organothallium compounds of the type $ArTl(OOCR)_2$. We are therefore able to prepare organothallium compounds of the type $ArTl(OOCR)_2$ by two independent methods and to identify them.

EXPERIMENTAL

Thallation of benzene. As we have already reported [5], heating of thallium triisobutyrate with excess of benzene gives a 90% yield of phenylthallium diisobutyrate, m.p. 221°. This substance is extremely soluble in pyridine and is readily soluble in methanol, ethanol, acetone, ethyl acetate, and chloroform; in benzene it is moderately soluble cold and extremely soluble hot; in dichloroethane it is sparingly soluble cold and moderately soluble hot; it is sparingly soluble in ether, even when hot, and it is insoluble in petroleum ether; it is insoluble in cold water, but is slightly soluble in hot water. Treatment of phenylthallium diisobutyrate with mercuric chloride in boiling alcoholic solution and subsequent acidification

*See the next paper in this journal.

with hydrochloric acid gave phenylmercury chloride, m.p. 256° (the literature [7] gives 258°).

Thallation of toluene. A mixture of 2.35 g (0.005 mole) of thallium triisobutyrate and 5 g (0.01 mole) of toluene was heated to boiling in the course of one hour, and the reaction mixture was set aside in an open vessel to crystallize. On the next day the precipitate was filtered off at the pump and washed with petroleum ether. The yield of crystalline substance, m.p. 171-172°, was 1.3 g (55%). After three recrystallizations (twice from dichloroethane and once from xylene) the melting point was raised to 185--186°.

Found %: Tl 43.01, 43.14. $C_{15}H_{21}TlO_4$.

Calculated %: Tl 43.50.

The thallation product was found to be a mixture of isomers. Its treatment with mercuric chloride under the conditions described in the account of the previous experiment led mainly to the formation of p-tolylmercury chloride, m.p. 222°*, which indicates the predominance of the p-isomer in the original product (the literature [7] gives m.p. 238.5°).

Thallation of naphthalene. A mixture of 4.65 g of thallium triisobutyrate and 8 g (sixfold excess) of naphthalene was heated for one hour at 112-115°. On the next day the product, which had solidified, was treated with ether: the undissolved part weighed 2.7 g. Recrystallization from dichloroethane gave 1.25 g (25%), m.p. 209°.

Found %: Tl 40.53, 39.80. $C_{18}H_{21}TlO_4$.

Calculated %: Tl 40.40.

A mixture of this substance with known 2-naphthylthallium diisobutyrate prepared by another method (see the next paper) melted without depression**.

Reaction of the diisobutyrate with mercuric chloride under the usual conditions gave 2-naphthylmercury chloride, m.p. 270°*** [7].

Thallation of anisole. As previously described, heating of thallium triisobutyrate with excess of anisole in a water bath for 30-40 minutes gives a 40% yield of p-methoxyphenylthallium diisobutyrate, m.p. 195°, identical with the product that we obtained from bis-p-methoxyphenylmercury and thallium triisobutyrate (m.p. 196°). p-Methoxyphenylthallium diisobutyrate is extremely soluble in pyridine, readily soluble in methanol, and somewhat less soluble in ethanol (the solution darkens), moderately soluble in the cold in ethyl acetate and chloroform (much more soluble hot), and sparingly soluble in acetone (more soluble hot). In benzene, dichloroethane, and carbon tetrachloride p-methoxyphenylthallium diisobutyrate is sparingly soluble cold, but moderately soluble hot. It is insoluble in diethyl ether, petroleum ether, and water. When a solution of 0.5 g of p-methoxyphenylthallium diisobutyrate in 12 ml of methanol is boiled for 15 minutes with 0.7 g of mercuric bromide (in 5 ml of methanol) and the product is decomposed with hydrobromic acid, 2 g of a precipitate is obtained; it has a constant melting point of 250-250.5° (from benzene).

Found %: Br 20.82 (by Stepanov's method). C_7H_7BrHgO.

Calculated %: Br 20.67.

As the literature [8] gives a lower melting point for p-methoxyphenylmercury bromide (187°), we prepared it by two independent methods: 1) heating of 0.41 g of bis-p-methoxyphenylmercury with an equimolecular amount (0.36 g) of mercuric bromide in 125 ml of alcohol gave 0.65 g of precipitate, m.p. 249-250° (from benzene); 2) a mixture of 0.41 g of bis-p-methoxyphenylmercury and an equimolecular amount (0.37 g) of mercuric isobutyrate was heated in 60 ml of boiling acetone for 30 minutes. Acetone was distilled off and the residue was treated with an aqueous-alcoholic solution of sodium bromide. The precipitate was filtered off at the pump and washed, first with water and then with alcohol. The pro-

*The melting points of m- and o-tolylmercury chlorides are 160° and 146°, respectively.

**The melting point of 1-naphthylthallium diisobutyrate is 183-184°.

***The melting point of 1-naphthylmercury chloride is 193° [7].

duct melted at 249-250° (from acetone). No depression was observed in mixture tests on these two preparations of p-methoxyphenylmercury bromide and the preparation obtained from p-methoxyphenylthallium diisobutyrate.

Thallation of phenetole. A mixture of 5 g of thallium triisobutyrate and 6 g (an excess) of phenetole was heated for one hour in a water bath. On the next day the precipitate was filtered off at the pump and washed with petroleum ether. The yield of p-ethoxyphenylthallium diisobutyrate was 1.2 g (23%). After being recrystallized from dichloroethane with an addition of petroleum ether, it melted at 186.5°.

Found %: Tl 40.93, 40.63. $C_{16}H_{23}TlO_5$.

Calculated %: Tl 40.88.

Treatment of this product with mercuric chloride under the usual conditions gave p-ethoxyphenyl mercury chloride, m.p. 244° (the literature [7] gives 249°).

p-Ethoxyphenylthallium diisobutyrate is a white crystalline substance, stable in air. It is very readily soluble in pyridine and methanol, somewhat less soluble in ethanol and chloroform, and moderately soluble in ethyl acetate; in acetone, benzene, and dichloroethane it is sparingly soluble cold, but moderately soluble hot; it is sparingly soluble in carbon tetrachloride, diethyl ether, and petroleum ether.

Thallation of o-dimethoxybenzene. A mixture of 4.65 g (0.01 mole) of thallium triisobutyrate and 4 g of o-dimethoxybenzene (150% excess) was heated in a boiling water bath for 45 minutes in all; after 10 minutes solution was complete, and in the succeeding 10-15 minutes the whole of the reaction mixture solidified. On the next day the product was washed with petroleum ether on a filter. Yield 3.65 g (75%), m.p. 186-187° (188° after recrystallization from dichloroethane).

Found %: Tl 39.77, 39.47. $C_{16}H_{23}TlO_6$.

Calculated %: Tl 39.61.

The diisobutyrate is a white crystalline substance, stable in air. It is readily soluble in chloroform, methanol, ethanol (a little alcoholysis occurs), and pyridine; it dissolves readily when heated in ethyl acetate and benzene, but somewhat less readily in dichloroethane; it is sparingly soluble in acetone and carbon tetrachloride, and insoluble in diethyl ether and petroleum ether.

In order to determine the position taken up by thallium in the nucleus the compound was treated with iodine: 5.7 g (0.011 mole) of the diisobutyrate was treated with 2.9 g (0.011 mole) of iodine in chloroform. On the next day the reaction mixture was treated with sulfur dioxide (decolorization). It was then filtered, the filtrate was extracted with petroleum ether, and the extract was washed with 5% sodium carbonate solution and then with water. The extract was dried with calcium chloride, and solvent was distilled off. Cooling of the oily residue gave 2.4 g of a crystalline substance of m.p. 34-35°. According to the literature [9], 4-iodo-1,2-dimethoxybenzene melts at 34-35°.

It is therefore proved that in the thallation of o-dimethoxybenzene thallium enters the 4-position.

Thallation of m-dimethoxybenzene. A mixture of 4.65 g of thallium triisobutyrate and 2.5 g (100% excess) of m-dimethoxybenzene was heated for 45 minutes in a boiling water bath. When cool, the product was treated with a 1 : 1 mixture of diethyl ether and petroleum ether; the undissolved residue was filtered off at the pump and washed with petroleum ether. Yield 3.8 g (73%); m.p. 147-148° (unchanged by recrystallization from benzene with an addition of petroleum ether).

Found %: Tl 39.59, 39.56. $C_{16}H_{23}TlO_6$.

Calculated %: Tl 39.61.

This diisobutyrate is a white crystalline substance, readily soluble in chloroform, dichloroethane, and pyridine. It is somewhat less soluble in carbon tetrachloride, in which it is much more soluble hot than cold; it dissolves better also in hot methanol, ethanol, acetone, and ethyl acetate (a slight brown coloration appears); it is insoluble in petroleum ether and diethyl ether (in the latter solvent a slight brown coloration occurs).

Thallation of p-dimethoxybenzene. A mixture of 2.5 g (90% excess) of p-dimethoxybenzene and 4.65 g of thallium triisobutyrate was heated at 95-105° for 105 minutes. On the next day the solid mass was treated with a 1 : 1 mixture of diethyl ether and petroleum ether, and washing of the insoluble part with petroleum ether gave 2.8 g (54%) of a substance of m.p. 104-106°. Recrystallization from benzene with an addition of petroleum ether gave 2.2 g (43%), m.p. 112-113°.

Found %: Tl 39.35, 39.10. $C_{16}H_{23}TlO_6$.

Calculated %: Tl 39.61.

This diisobutyrate is a white crystalline substance, readily soluble in methanol, acetone, benzene, chloroform, dichloroethane, carbon tetrachloride, and pyridine; it is readily soluble also in ethyl acetate and ethanol (slight alcoholysis); it is sparingly soluble in diethyl ether and petroleum ether.

Thallation of 1,3,5-trimethoxybenzene. A mixture of 0.7 g (70% excess) of 1,3,5-trimethoxybenzene (m.p. 49° after steam distillation and crystallization from petroleum ether) and 1.4 g of thallium triisobutyrate was heated for 30 minutes in a boiling water bath. The resulting homogeneous viscous liquid did not crystallize when cooled. Addition of petroleum ether gave a white crystalline substance, m.p. 108-109°, in a yield of 1.4 g (87.5%). After recrystallization from carbon tetrachloride with an addition of petroleum ether, the melting point was 117-118°, which was not changed by recrystallization from the same mixture of solvents. The substance was kept in a desiccator over sulfuric acid (slight hydrolysis occurred in the air).

Found %: Tl 37.13, 37.31. $C_{17}H_{25}TlO_7$.

Calculated %: Tl 37.43.

1,3,5-Trimethoxyphenylthallium diisobutyrate is a slightly creamy substance. It is very readily soluble in methanol, ethanol, benzene, dichloroethane, chloroform, ethyl acetate, and pyridine; it is sparingly soluble in carbon tetrachloride in the cold, but better hot; it is very sparingly soluble in diethyl ether and petroleum ether.

Thallation of thiophene. As already reported briefly [5], thiophene is extremely readily thallated by thallium triisobutyrate (5 minutes in a water bath; yield 88%). 2-Thienylthallium diisobutyrate is a white crystalline substance, m.p. 215-216°*, unchanged by admixture of 2-thienylthallium diisobutyrate prepared from di-2-thienylmercury and thallium triisobutyrate. The substance is very readily soluble in methanol, pyridine, and ethyl acetate, and it is somewhat less soluble in ethanol and acetone (in these two solvents yellowing of the solution occurs). When the product is dissolved in chloroform, dichloroethane, and carbon tetrachloride (in which it is fairly soluble) some turbidity remains. It is insoluble in diethyl ether and petroleum ether. The entry of thallium into the 2-position is proved by reaction with mercuric bromide, in which 2-thienylmercury bromide is formed [5].

Thallation of acetophenone. A mixture of 4.65 g (0.01 mole) of thallium triisobutyrate and 4.5 g (excess) of acetophenone was heated for five minutes at about 100°. On the next day the precipitate formed was filtered off at the pump and washed with petroleum ether. Yield 2 g (45.5%); m.p. 127-128°. The substance was analyzed in this form, as it was not found possible to recrystallize it.

Found %: Tl 46.04. $C_{24}H_{34}Tl_2O_9$.

Calculated %: Tl 46.68.

Determination of the number of acid groups gave the value 3.96.

The product, phenacylidenedithallium tetraisobutyrate, is a white crystalline substance, not very stable in the air, but stable when kept in a desiccator over sulfuric acid. It is very readily soluble in methanol and pyridine, and it is rather less soluble in chloroform; it is very readily soluble in hot dichloroethane. However, we did not succeed in recovering the substance from its solution in these solvents.

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*The melting point of 2-thienylthallium diisobutyrate is 215-216°, and not 209-210°, as erroneously reported previously [5].

In ethanol, acetone, and ethyl acetate it decomposes slightly (turns brown). It is insoluble in benzene, carbon tetrachloride, diethyl ether, and petroleum ether.

The thallium-carbon bonds of the substance were subjected to attack by bromine in the following way. The above-described tetraisobutyrate (2 g) was sprinkled slowly into a solution of 1.3 g of bromine and 2 g of potassium bromide in 5 ml of water; a reddish oil then began to appear at the bottom of the vessel. The reaction mixture was treated with sulfur dioxide solution and was then extracted with ether. The ether layer, after being washed and dried as usual, was allowed to evaporate. After long standing the oil crystallized (m.p. 35°) (for 2,2-dibromoacetophenone the literature [10] gives m.p. 35-36°).

Thallation of dibenzofuran. The thallation of dibenzofuran, carried out by treating excess of the latter with thallium triisobutyrate, gives a dibenzofuranylthallium diisobutyrate of m.p. 204-205°. In view of the difference between our results and those of Gilman [4], this matter will be the subject of a separate paper.

SUMMARY

1. For the first time a description is given of the thallation of organic compounds by tervalent thallium salts of organic acids with formation of $ArTlX_2$ (X is the residue of an organic acid).

2. The thallation of benzene, toluene, naphthalene, anisole, phenetole, o-, m-, and p-dimethoxybenzenes, 1,3,5-trimethoxybenzene, thiophene, acetophenone, and dibenzofuran was found to proceed under mild conditions with good yield.

3. The orientation of thallation was determined, and the difficulty with which polythallation occurs was noted.

4. Thallation and the reaction that we have discovered* between diarylmercurys and tervalent thallium salts of organic acids provide new methods for the synthesis of compounds of the type $ArTlX_2$.

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REACTION OF DIARYLMERCURYS WITH TERVALENT THALLIUM SALTS AS A METHOD FOR THE SYNTHESIS OF COMPOUNDS OF THE TYPE $ArTlX_2$

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Organothallium compounds of the type $ArTlX_2$ (X is halogen) have been studied very little. The reasons for this are, first, absence of convenient methods for preparing them* and, second, their comparative instability (tendency to undergo disproportionation or decomposition in other ways). The only practicable method of synthesis that we can cite is that of Challenger [1]: it consists in 1) preparation of an organomagnesium compound, 2) conversion of this into an organoboron acid, and 3) reaction of this acid with a thallium trihalide in accordance with the equation:

$$C_6H_5B(OH)_2 + TlX_3 + H_2O \rightarrow C_6H_5TlX_2 + HX + H_3BO_3 \qquad (1)$$

The process of preparing $ArTlX_2$ is therefore a three-stage one, even if we do not consider the further treatment of the areneboronic acids for the preparation of compounds with substituents in the aromatic nucleus.

Challenger's method was later applied in various cases by Nametkin, Melnikov, and co-workers [2] and was supplemented by an accessory (in the sense that it operates with already prepared organothallium compounds) process [3] based on reversed disproportionation. These authors described various organothallium compounds $ArTlX_2$ (X is halogen). They were yellow, orange, and dark-brown substances**, unstable under the action of light, prone to undergo reactions of the type $2RTlX_2 \rightleftharpoons R_2TlX + TlX_3 \rightarrow TlX + 2RX$, and contaminated with inorganic thallium salts (not removable by crystallization). They became more intense in color when treated with ether, etc.

Our successful attempts [5] to work with organic salts of metals in organometallic chemistry prompted us to use organic salts of tervalent thallium in the synthesis of organothallium compounds of the type $ArTlX_2$ [4]. We considered that the replacement of halogen by the residue of an organic acid would render the synthesis more convenient in various ways and would lead to compounds of higher stability.

We based our method of synthesizing $ArTl(OOCR)_2$ on reaction between the quite accessible organic salts of tervalent thallium and diarylmercurys, which, thanks to Nesmeyanov's method [6], are also readily accessible***.

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*See preceding paper in this journal.

**According to Challenger and Parker [1], phenylthallium dichloride is colorless.

***In some cases we carried out the symmetrization of ArHgX with the aid of sodium borohydride.

The reaction proceeds smoothly according to the equation:

$$Ar_2Hg + Tl(OOCR)_3 \rightarrow ArTl(OOCR)_2 + ArHgOOCR. \quad (2)$$

In previously described cases [7-10] of reaction between diaryl- or dialkyl-mercurys and thallium trichloride, compounds of the type Ar_2TlX have been obtained; hence, reaction in accordance with equation (2) was observed for the first time by us.

The reaction is carried out as follows. Equivalent amounts of the diarylmercury and tervalent thallium salt* are mixed in chloroform solution and heated for a short time at the boiling point of the solvent. Completion of the process is indicated by the disappearance of the thallium salt: the product is not appreciably hydrolyzed by water, whereas tervalent thallium salts of organic acids are known to give a brown coloration with water owing to the formation of thallium oxide. The mixture is left to the next day for completion of reaction. The compound $ArTl(OOCR)_2$ is the first to be precipitated, and the organomercury compound remains in solution. Yields of 50-90% of $ArTl(OOCR)_2$ are obtained.

The following compounds were prepared in this way: phenylthallium diisobutyrate (m.p. 221°), p-tolylthallium diisobutyrate (m.p. 200°), 1-naphthylthallium diisobutyrate (m.p. 184°), 2-naphthylthallium diisobutyrate (m.p. 209°), 2-thienylthallium diisobutyrate (m.p. 215°), p-chlorophenylthallium diisobutyrate (m.p. 229°), p-bromophenylthallium diisobutyrate (m.p. 219°). It will be seen that the melting points are fairly high, though lower than those of the corresponding compounds of the type $Ar_2TlOOCR$.

Compounds of the type $ArTl(OOCR)_2$, which we have now prepared for the first time, are stable substances, having no tendency to undergo disproportionation or other decomposition; they are not readily hydrolyzed. They are soluble in most organic solvents and can readily be crystallized. Unlike the products of formula $ArTlX_2$ (X is halogen) obtained by Nametkin and Melnikov, these new compounds are colorless. In order to show that the color is not dependent on the presence of the halide anion, but is probably a result of the method of preparation in an aqueous medium with participation of a thallium halide, we brought about the replacement of the organic acid residue of $ArTl(OOCR)_2$ by halide by various methods under mild conditions: no colored compounds were obtained.

It should be noted that by reaction between two molecular proportions of the diarylmercury and one of the tervalent thallium salt of the organic acid it is possible to obtain [4] organothallium compounds of the type $Ar_2TlOOCR$:

$$2Ar_2Hg + Tl(OOCR)_3 \rightarrow Ar_2TlOOCR + 2ArHgOOCR \quad (3)$$

Also, from $Ar_2TlOOCR$ and a tervalent thallium salt we may readily obtain $ArTl(OOCR)_2$ [4]:

$$Ar_2TlOOCR + Tl(OOCR)_3 \rightarrow 2ArTl(OOCR)_2. \quad (4)$$

The literature [11] describes also some organothallium compounds of the type $Ar_2TlOOCR$ obtained by another method: from Ar_2TlBr, silver oxide, and the organic acid. As the reaction was generally carried out in presence of excess of organic acid, most of these were described in the form of their acid salts.

In the paper immediately preceding the present paper in this journal, we described still another method of preparing organothallium compounds of the type $ArTl(OOCR)_2$, namely, the direct thallation of organic compounds. We therefore have two independent methods of preparing members of the same class of compounds, which enables us to confirm their identities. The preparation of the thallium triisobutyrate used as starting material has been described by us previously [4]. The compounds ArHgOOCR, which we obtained as by-products, were converted in the usual way into the corresponding chlorides and identified in that form.

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*It is convenient to use thallium triisobutyrate, but salts of other organic acids may be used.

EXPERIMENTAL

Phenylthallium diisobutyrate. As we have already reported in a preliminary communication [4], diphenylmercury and thallium triisobutyrate react in equimolecular proportions in hot chloroform solution with formation in the course of 30 minutes of phenylthallium diisobutyrate, m.p. 221-222°, in 87.9% yield. Phenylmercury isobutyrate is formed at the same time and is easily separated. Boiling of phenylthallium diisobutyrate with mercuric chloride in alcoholic solution and subsequent acidification with hydrochloric acid give phenylmercury chloride, m.p. 258° (the literature [6] gives m.p. 258°).

Diphenylthallium isobutyrate. As we have already reported in a preliminary communication [4], diphenylmercury (2 moles) and thallium triisobutyrate (1 mole) react in chloroform solution with formation of diphenylthallium isobutyrate, m.p. 241° (from dichloroethane). Diphenylthallium isobutyrate is stable in the air. It is insoluble in water, very readily soluble in pyridine, readily soluble in methanol, but somewhat less readily in ethanol. In ethyl acetate it is moderately soluble cold, but readily soluble hot; in benzene and acetone it is sparingly soluble cold, but readily soluble hot; in dichloroethane it is sparingly soluble cold and moderately soluble hot; it is insoluble in carbon tetrachloride and petroleum ether, even hot. Under the conditions described above, treatment with mercuric chloride gives phenylmercury chloride.

p-Tolylthallium diisobutyrate. A solution of 4.65 g (0.01 mole) of thallium triisobutyrate in 8 ml of chloroform was mixed with a suspension of 3.82 g (0.01 mole) of di-p-tolylmercury in 15 ml of chloroform. Almost complete dissolution occurred; the mixture was filtered and set aside overnight. About one-half of the solvent was evaporated off, and the precipitate formed was filtered off at the pump and washed with petroleum ether. Yield 2.05 g (43.7%); m.p. 199.5-200° after recrystallization from dichloroethane.

Found %: Tl 43.78, 43.50. $C_{18}H_{21}TlO_4$.

Calculated %: Tl 43.49

p-Tolylthallium diisobutyrate is a white crystalline substance, stable in the air. It is extremely soluble in pyridine, readily soluble in methanol, ethanol, acetone, and chloroform, and somewhat less soluble in ethyl acetate. In benzene, carbon tetrachloride, and dichloroethane it is sparingly soluble cold, but moderately soluble hot; it is insoluble in diethyl ether, petroleum ether, and water. By reaction with mercuric chloride in alcoholic solution under the usual conditions it gives p-tolylmercury chloride, m.p. 233° (the literature [6] gives m.p. 238-239°).

Di-p-tolylthallium isobutyrate. A solution of 2.35 g (0.005 mole) of thallium triisobutyrate was prepared by heating it with 6 ml of chloroform, and a suspension of 3.82 g (0.01 mole) of di-p-tolylmercury in 10 ml of chloroform was added. Part of the suspended matter dissolved, and the mixture was heated until solution was complete. The solution was set aside to cool, and the precipitate that formed was filtered off at the pump and washed with petroleum ether; yield 1.8 g (76%). After being recrystallized from dichloroethane, di-p-tolylthallium isobutyrate melted with decomposition at 244-244.5°.

Found %: Tl 42.87, 42.91. $C_{18}H_{21}TlO_2$.

Calculated %: Tl 43.13.

This isobutyrate is a white crystalline substance, stable in the air. It is extremely soluble in pyridine and methanol and fairly soluble in chloroform. It is readily soluble hot in dichloroethane and somewhat less soluble hot in ethanol and acetone. It is sparingly soluble, even hot, in ethyl acetate, benzene, carbon tetrachloride, diethyl ether, and petroleum ether. By reaction under the usual conditions with mercuric chloride, it gives p-tolylmercury chloride.

1-Naphthylthallium diisobutyrate. A solution of 4.65 g (0.01 mole) of thallium triisobutyrate in 7 ml of chloroform was added to a suspension of 4.54 g (0.01 mole) of di-1-naphthylmercury in 10 ml of the same solvent. The reaction mixture was heated until the precipitate had dissolved completely. Some solvent was evaporated, and the cooled solution then gave a crystalline precipitate, which was filtered off at the pump and washed with petroleum ether; yield 4.2 g. Recrystallization from carbon tetrachloride gave 2.4 g (47.5%), m.p. 183-184°.

Found %: Tl 39.93, 39.86. $C_{18}H_{21}TlO_4$.

Calculated %: Tl 40.40.

1-Naphthylthallium diisobutyrate is a white crystalline substance, stable in the air. It is extremely soluble in methanol and ethanol (slight alcoholysis), very readily soluble in ethyl acetate, acetone, chloroform, benzene, dichloroethane, and pyridine, less soluble in carbon tetrachloride, and insoluble in diethyl ether and petroleum ether. By reaction under the usual conditions with mercuric chloride it gives 1-naphthylmercury chloride, m.p. 190° (the literature [6] gives 191°).

2-Naphthylthallium diisobutyrate. A solution of 2.33 g (0.005 mole) of thallium triisobutyrate in 8 ml of chloroform was mixed with a suspension of 2.27 g (0.005 mole) of di-2-naphthylmercury in 10 ml of chloroform. The reaction mixture was heated to boiling and then cooled; the precipitate was filtered off at the pump; yield 2.3 g (91%); m.p. 205-206°, raised to 209-210° by recrystallization from dichloroethane.

Found %: Tl 40.22, 40.16. $C_{18}H_{21}TlO_4$.

Calculated %: Tl 40.39.

2-Naphthylthallium diisobutyrate is a white crystalline substance, stable in the air. It is very soluble in pyridine, fairly soluble hot, but sparingly cold in methanol, acetone, ethyl acetate, benzene, chloroform, and dichloroethane, and sparingly soluble in diethyl ether, petroleum ether, and carbon tetrachloride. In ethanol slight alcoholysis occurs, so that the solution yellows. The presence in the mother liquor of an equivalent amount of 2-naphthylmercury isobutyrate was proved by its conversion into 2-naphthylmercury chloride, m.p. 269-270° (the literature [6] gives m.p. 270°).

p-Methoxyphenylthallium diisobutyrate. As we have already reported in a preliminary communication [4], heating of equimolecular amounts of bis-p-methoxyphenylmercury and thallium triisobutyrate in a chloroform medium gives a 65% yield of p-methoxyphenylthallium diisobutyrate, m.p. 196° (from dichloroethane). As already noted [4], reaction of this with mercuric chloride under the usual conditions gives p-methoxyphenylmercury chloride.

Bis-p-methoxyphenylthallium isobutyrate. A solution of 2.35 g (0.005 mole) of thallium triisobutyrate in 10 ml of chloroform was added to a suspension of 4.15 g (0.01 mole) of bis-p-methoxyphenylmercury in 10 ml of chloroform, and the mixture was heated until solution was complete. Some solvent was allowed to evaporate in the cold, and the precipitate that formed was filtered off at the pump, washed with petroleum ether, and recrystallized from dichloroethane; yield 2 g (66%); m. p. 246°, raised to 252° by recrystallization from the same solvent.

Found %: Tl 39.70, 39.62. $C_{18}H_{21}TlO_4$.

Calculated %: Tl 40.40.

Bis-p-methoxyphenylthallium isobutyrate is a white substance, stable in the air. It is extremely soluble in pyridine, and is moderately soluble cold and readily soluble hot in methanol and ethanol; it is sparingly soluble in benzene, acetone, ethyl acetate, carbon tetrachloride, ether, and petroleum ether. As noted previously [4], when boiled with alcoholic mercuric chloride it gives p-methoxyphenylmercury chloride.

2-Thienylthallium diisobutyrate. A mixture of 4.2 g (0.009 mole) of thallium triisobutyrate in 10 ml of chloroform and 3.4 g (0.009 mole) of di-2-thienylmercury in 30 ml of chloroform was heated at boiling until solution was complete. The solution was filtered, and some of the chloroform was evaporated off. A precipitate formed and was filtered off and washed with petroleum ether; yield 2.8 g (67.3%); after being recrystallized from dichloroethane it melted at 216-217°.

Found %: Tl 44.71, 44.32. $C_{12}H_{17}O_4STl$.

Calculated %: Tl 44.25.

2-Thienylthallium diisobutyrate is a white crystalline substance, stable in the air. It is extremely soluble in methanol, ethyl acetate, chloroform, dichloroethane, carbon tetrachloride, benzene, and pyridine (a slight turbidity remains); it dissolves readily in ethanol and acetone, but there is slight yellowing; it is insoluble in diethyl ether and petroleum ether.

p-Chlorophenylthallium diisobutyrate. A solution of 4.65 g (0.01 mole) of thallium triisobutyrate in 15 ml of chloroform was added to 4.25 g (0.01 mole) of bis-p-chlorophenylmercury pasted with 15 ml of chloroform (the bis-p-chlorophenylmercury then began to go into solution until there remained only a small amount, which was dissolved by warming). Some of the chloroform was evaporated off, and the precipitate that formed was filtered off and washed with petroleum ether. Recrystallization from dichloroethane gave 3 g of a substance of m.p. 229° (with decomposition) and 0.6 g of a substance of m.p.224-225°; the yield of recrystallized product was 73.5%.

Found %: Tl 41.15, 41.21. $C_{14}H_{18}TlO_4Cl$.

Calculated %: Tl 41.67.

p-Chlorophenylthallium diisobutyrate is a white substance, readily soluble in pyridine, methanol, and ethanol, readily soluble hot but sparingly in the cold in benzene, ethyl acetate, chloroform, dichloroethane, and carbon tetrachloride, sparingly soluble, even hot, in diethyl ether and petroleum ether.

p-Chlorophenylthallium dichloride. p-Chlorophenylthallium diisobutyrate (1 g) was dissolved in 25 ml of methanol, excess of aqueous ammonia was added, the mixture was allowed to stand for 30 minutes and then diluted with water, and the precipitate formed was filtered off and washed with water (0.8 g of product). This product was then pasted with 12 ml of methanol, and the calculated amount of alcoholic hydrogen chloride was added. The product, amounting to 0.65 g, was p-chlorophenylthallium dichloride, a white substance, m.p. 252° (it was not crystallized: the substance is sparingly soluble in the usual organic solvents, and when heated with them it decomposes).

Found %: Tl 52.07, 52.79. $C_6H_4TlCl_3$.

Calculated %: Tl 52.78.

According to the literature [2] it is a lemon-yellow substance, m.p. about 250°.

p-Bromophenylthallium diisobutyrate. As already reported in a preliminary communication [4], reaction between equimolecular amounts of bis-p-bromophenylmercury and thallium triisobutyrate in chloroform solution gives a 50% yield of p-bromophenylthallium diisobutyrate, m.p. 219° (with decomposition). The product is a white crystalline substance, stable in the air. It is extremely soluble in pyridine, readily soluble in methanol, ethanol, acetone, ethyl acetate, and chloroform, sparingly soluble cold but moderately soluble hot in dichloroethane and carbon tetrachloride, sparingly soluble cold but readily hot in benzene, and insoluble in diethyl ether, petroleum ether, and water.

p-Bromophenylthallium dichloride. As already reported in a preliminary communication [4], treatment of p-bromophenylthallium diisobutyrate with alcoholic hydrogen chloride gives p-bromophenylthallium dichloride, a white crystalline substance, m.p. 261° (from ethyl acetate). According to the literature [2] it forms yellow-orange crystals, m.p. 262-263°.

SUMMARY

1. A new method was found for the synthesis of organothallium compounds of the type $ArTlX_2$. It is based on reaction between a diarylmercury and the tervalent thallium salt of an organic acid.

2. Compounds of the type $ArTlX_2$ (X is the residue of an organic acid) were prepared and characterized for the first time, the substances obtained being phenyl-, p-tolyl-, 1-naphthyl-, 2-naphthyl-, 2--thienyl-, p-chlorophenyl-, p-bromophenyl-, and p-methoxyphenyl-thallium isobutyrates.

3. It was shown that, by reaction between diarylmercurys and tervalent thallium salts taken in molar proportions of 2 : 1, compounds of the type $Ar_2TlOOCR$ are formed smoothly.

4. It was shown that reaction between compounds of the types $Ar_2TlOOCR$ and $Tl(OOCR)_3$ leads to the formation of $ArTl(OOCR)_2$.

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SOME REACTIONS OF ORGANOSILICON COMPOUNDS HAVING FUNCTIONAL GROUPS IN THE α- AND γ-POSITIONS WITH RESPECT TO THE SILICON ATOM

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In a previous investigation [1] we established that, in reactions with potassium iodide, the chlorine of (chloromethyl) trimethylsilane (I) is considerably more mobile than that of (3-chloropropyl)trimethylsilane (II). In the present investigation we attempted to compare the relative reactivities of compounds of the type $R_3Si(CH_2)_nX$ in some other reactions (n is 1 or 3, X is one of the functional groups Cl, SCN, $N(C_2H_5)_2$, or O_2CCH_3).

With this object a mixture of equal amounts (0.3 mole each) of the α- and γ-chloro compounds (I) and (II) were treated with 0.3 mole of NaSCN. It was found that mainly the α-chloro compound reacted, almost the whole of the γ-compound (II) being recovered unchanged

$$(CH_3)_3SiCH_2Cl + (CH_3)_3SiCH_2CH_2CH_2Cl + NaSCN \rightarrow$$
$$\rightarrow (CH_3)_3SiCH_2SCN + (CH_3)_3SiCH_2CH_2CH_2Cl,$$

i.e. in this reaction the halogen of the α-chloro compound (I) is more reactive than that of the γ-chloro compound (II), which is fully in accord with the results obtained in the analogous reaction of the same compounds (I) and (II) with KI. Different results were obtained when potassium acetate was used under similar conditions. It was then found that the γ-chloro compound (II) reacted to the extent of 75% and the α-chloro compound (I) to the extent of 54.7 % (48% of the γ-acetate and 33.4 % of the α-acetate were obtained). Hence, in reaction with potassium acetate, the γ-chloro compound (II) is somewhat more reactive than the α-chloro compound (I). The probable explanation of this result is that the reaction mechanism differs from that operating in the reactions of the α- and γ-chloro compounds (I) and (II) with KI or NaSCN.

The difference in reactivity between the α- and γ-chloro compounds is shown also in their reactions with quinoline. α-Chloro compounds undergo some dehydrochlorination when treated with quinoline; though reaction proceeds only to a slight extent [2]; on the other hand, γ-chloro compounds, such as $Cl_3SiCH_2CH_2CH_2Cl$, $CH_3Cl_2SiCH_2CH_2CH_2Cl$, and $CH_3Cl_2SiCH_2CH_2CH(CH_3)CH_2Cl$, are not dehydrochlorinated at all by quinoline. An attempt to eliminate HCl from γ-chloro tetrasubstituted silanes by means of alcoholic alkali did not result in dehydrochlorination, but in the formation of ethers, which may be obtained also by treating the same γ-chloro compounds with sodium alkoxides:

$$(CH_3)_3SiCH_2CH_2CH_2Cl \xrightarrow[NaOR]{NaOH + ROH} (CH_3)_3SiCH_2CH_2CH_2OR.$$

It should be noted that secondary α-chloro compounds ($R_3SiCHClCH_3$) are dehydrochlorinated under the same conditions [3] with formation of $R_3SiCH=CH_2$, a fact that we confirmed once more by treating a mixture of $(CH_3)_3SiCHClCH_3$ and $(CH_3)_3SiCH_2CH_2CH_2Cl$ with alcoholic alkali. Only pyrolysis in presence of activated charcoal at 600° was effective in eliminating HCl from the γ-chloro compound

($CH_3Cl_2SiCH_2\underset{\displaystyle CH_2}{\underset{|}{C}}HCH_2Cl$). On the basis of spectroscopic data *, it may be concluded that this reaction proceeded as follows:

$$(CH_3)Cl_2SiCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2Cl \rightarrow \begin{cases} CH_3Cl_2SiCH_2C(CH_3)=CH_2 \\ CH_3Cl_2SiCH=C(CH_3)_2 \\ CH_3Cl_2SiCH_2CH=CHCH_3 \end{cases}$$

However, the pyrolysis of a γ-acetate resulted in the formation of only one compound, which had a β-double bond

$$(CH_3)_3SiCH_2CH_2CH_2O_2CCH_3 \xrightarrow{500^\circ} (CH_3)_3SiCH_2CH=CH_2 + HO_2CCH_3.$$

The absence of even traces of trimethylpropenylsilane was shown by Raman analysis*.

In the present investigation we synthesized some new γ-chloro compounds and also four new γ-thiocyanato compounds, the synthesis of the first of which we reported previously [4]. In an attempt to convert α- and γ-thiocyanato compounds by a known reaction [5] into the corresponding sulfonyl chlorides,

$$RSCN \xrightarrow{Cl_2+H_2O} RSO_2Cl,$$

we found that when R is $(CH_3)_3SiCH_2$ chlorine is vigorously absorbed, but scission of the Si—C bond probably occurs and the corresponding sulfonyl chloride cannot be isolated. When, however, R is $(CH_3)_3SiCH_2CH_2CH_2$, chlorine does not react with the thiocyanate. Trimethyl(thiocyanatomethyl)silane dissolves in concentrated sulfuric acid, and the solution, when poured into water, gives a crystalline product, which, according to Riemschneider's reaction [6], should be the corresponding thiocarbamate. However, elementary analysis of these crystals was not in accord with the formula $(CH_3)_3SiCH_2SC(=O)NH_2$. Finally, by the usual method [7] we synthesized the γ-amine $(CH_3)_3SiCH_2CH_2CH_2N(C_2H_5)_2$ and showed that, unlike the α-amine $(CH_3)_3SiCH_2N(C_2H_5)_2$ [7], it reacts very slowly with ethyl iodide:

$$(CH_3)_3SiCH_2CH_2CH_2N(C_2H_5)_2 \xrightarrow{C_2H_5I} [(CH_3)_3SiCH_2CH_2CH_2\overset{+}{N}(C_2H_5)_3]I^-.$$

By transesterification, $(CH_3)_3SiCH_2CH(CH_3)CH_2O_2CCH_3$, like $(CH_3)_3SiCH_2O_2CCH_3$, readily gives the corresponding alcohol, which adds vigorously to acrylonitrile [8].

EXPERIMENTAL

The synthesis of γ-chloro compounds was effected by addition of RCl_2SiH (in which R is CH_3 or C_2H_5) to allyl or 2-methylallyl chloride under the conditions described previously [9], but in absence of nitrogen under pressure. In the preparation of $CH_3Cl_2SiCH_2CH(CH_3)CH_2Cl$ we isolated CH_3-i-$C_4H_9SiCl_2$. It must be mentioned that replacement of the platinized charcoal catalyst in these reactions by palladized charcoal or Raney nickel results in the formation of only the corresponding $RSiCl_3$, no γ-chloro compounds being formed. Finally, it was found that, unlike dichloromethylsilane CH_3Cl_2SiH, trichlorosilane $HSiCl_3$ does not add to allyl chloride in presence of platinized charcoal (2% Pt).

(3-Chloro-2-methylpropyl)trimethylsilane $ClCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2Si(CH_3)_3$. To CH_3MgCl prepared from 30 g of magnesium in 500 ml of ether, 106 g of dichloro(3-chloro-2-methylpropyl)methylsilane was added. The mixture was boiled for three hours and then treated with water. The ether layer was combined with

* The Raman spectra were determined and interpreted by Yu. P. Egorov.

ether extracts of the aqueous layer and dried with calcium chloride. Vacuum distillation gave 67.1 g (78%) of (3-chloro-2-methylpropyl)trimethylsilane, b.p. 50-53° (12 mm).

Found %: C 51.11, 51.28; H 10.53, 10.40; Cl 21.81, 21.52; Si 16.87, 17.03. $C_7H_{17}SiCl$.

Calculated %: C 51.02; H 10.40; Cl 21.52; Si 17.04.

(3-Chloro-2-methylpropyl)diethylmethylsilane $ClCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2Si(C_2H_5)_2CH_3$. To C_2H_5MgBr prepared from 15.8 g of magnesium and 75 g of ethyl bromide in 300 ml of ether, 51.4 g of dichloro(3-chloro-2-methylpropyl)methylsilane was added. The usual treatment gave 38 g (80%) of (3-chloro-2-methylpropyl)diethylmethylsilane, b.p. 54-56° (2 mm).

Found %: C 56.24, 55.98; H 10.91, 10.87; Si 14.35, 14.28; Cl 18.57, 18.58. $C_9H_{21}SiCl$.

Calculated %: C 56.06; H 10.97; Si 14.56; Cl 18.38.

In an attempt to prepare (3-chloro-2-methylpropyl)methyldipropylsilane by the above-described method, we isolated 1,3-bis(3-chloro-2-methylpropyl)-1,3-dimethyl-1,3-dipropyldisiloxane, b.p. 150° (2 mm), in 48.7% yield.

Found %: C 51.64, 51.44; H 9.53, 9.68; Si 15.09, 15.28; Cl 18.81, 19.03. $C_{16}H_{36}Si_2Cl_2O$.

Calculated %: C 51.71; H 9.77; Si 15.11; Cl 19.06.

TABLE

No.	Formula of Compound	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR Found	MR Calc.	Yield (%)
1	$CH_2Cl_2SiCH_2CH(CH_3)_2$	137.8 (735)	1.4325	1.0281	43.21	42.09	—
2	$(CH_3)_2SiCH_2CH(CH_3)CH_2Cl$	53 (12)	1.4380	0.8812	49.07	49.01	78
3	$CH_3(C_2H_5)_2SiCH_2CH(CH_3)CH_2Cl$	56 (2)	1.4531	0.9002	57.88	58.03	80
4	$C_2H_5(CH_3)_2SiCH_2CH_2CH_2Cl$	57 (10)	1.4420	0.8881	49.06	48.89	76.5
5	$[n\text{-}C_3H_7CH_2SiCH_2CH(CH_3)CH_2Cl]_2O$	150 (2)	1.4612	0.9762	114.7	114.0	48.7
6	$(CH_3)_2SiCH_2CH(CH_3)CH_2SCN$	101 (10)	1.4710	0.9239	56.46	56.53	32.5
7	$(C_2H_5)_2CH_3SiCH_2CH_2CH_2SCN$	87.5 (1.5)	1.4780	0.9331	61.08	60.92	76.7
8	$(n\text{-}C_3H_7)_2CH_3SiCH_2CH_2CH_2SCN$	116.5 (1)	1.4760	0.9181	70.46	70.42	75.1
9	$(C_2H_5)_2CH_3SiCH_2CH(CH_3)CH_2SCN$	87 (1.5)	1.4801	0.9320	65.65	65.55	35.3
10	$(CH_3)_2SiCH_2CH_2CH_2O_2CCH_3$	182.5 (727)	1.4218	0.8743	50.63	50.57	—
11	$(CH_3)_2SiCH_2CH(CH_3)CH_2O_2CCH_3$	75 (12)	1.4230	0.8710	55.05	55.20	34.5
12*	$(CH_3)_2SiCH_2CH_2CH_2OC_2H_5$	A 155—156 (735)	1.4141	0.7911	50.63	50.57	71
13	$(CH_3)_2SiCH_2CH_2CH_2OC_2H_5$	B 157.5 (743)	1.4141	0.7900	50.70	50.57	73.5
14	$(CH_3)_2SiCH_2CH(CH_3)CH_2OCH_3$	150.5 (756)	1.4178	0.7972	50.63	50.57	48.2
15**	$(CH_3)_2SiCH_2CH_2CH_2OCH_3$	140 (764)	1.4102	0.7898	45.65	45.40	60
16	$(CH_3)_2SiCH_2CH_2CH_2N(C_2H_5)_2$	192.5 (756)	1.4308	0.7836	61.85	61.87	32.2
17	$(CH_3)_2SiCH_2CH(CH_3)CH_2OH$	73.5 (12)	1.4334	0.8331	45.67	45.62	76.3
18	$(CH_3)_2SiCH_2CH(CH_3)CH_2OCH_2CH_2CN$	97 (1.5)	1.4380	0.8770	59.78	59.71	79.5

*The literature [10] gives: B.p. 155° (760 mm), n_D^{20} 1.4136, d_4^{20} 0.7921.

**The literature [10] gives: B.p. 139° (762 mm), n_D^{20} 1.4105, d_4^{20} 0.7921; [11] n_D^{20} 1.4112; d_4^{20} 0.7907.

(3-Chloropropyl)ethyldimethylsilane $ClCH_2CH_2CH_2SiC_2H_5(CH_3)_2$. To CH_3MgCl prepared from 10 g of magnesium, 35 g of dichloro(3-chloropropyl)ethylsilane was added. The usual treatment gave 21.5 g (76.5%) of (3-chloropropyl)ethyldimethylsilane, b.p. 55-57° (10 mm).

Found %: C 51.28, 51.13; H 10.41, 10.40; Cl 21.24, 21.48; Si 17.27, 17.24. $C_7H_{17}SiCl$.

Calculated %: C 51.02; H 10.40; Cl 21.51; Si 17.04.

Trimethyl(2-methyl-3-thiocyanatopropyl)silane $(CH_3)_3SiCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2SCN$. (3-Chloro-2-methylpropyl)trimethylsilane (32.9 g) was added to a solution of 18 g of NaSCN in 200 ml of ethanol. The solution was boiled for 84 hours with six overnight breaks. Alcohol was distilled off, and the residue was treated

with water. The organic layer was dried with calcium chloride, and vacuum distillation then gave 12.3 g (32.5%) of trimethyl(2-methyl-3-thiocyanatopropyl)silane, b.p. 100-101° (10 mm).

Found %: C 51.51, 51.51; H 9.16, 9.20; Si 14.89, 14.93; S 17.09, 16.86. $C_8H_{17}SiSN$.

Calculated %: C 51.27; H 9.14; Si 14.99; S 17.11.

Diethylmethyl(3-thiocyanatropropyl)silane $(C_2H_5)_2CH_3SiCH_2CH_2CH_2SCN$. A mixture of 200 ml of ethanol, 17 g of NaSCN, and 35.7 g of (3-chloropropyl)diethylmethylsilane [1] was boiled for 53 hours. The usual treatment gave 31 g (76.7%) of diethylmethyl(3-thiocyanatopropyl)silane, b.p. 85-88° (1.5 mm).

Found %: C 53.54, 53.51; H 9.52, 9.47; Si 13.99; 14.24; S 15.34; 15.76. $C_9H_{19}SiSN$.

Calculated %: C 53.67; H 9.50; Si 13.94; S 15.92.

Methyldipropyl(3-thiocyanatopropyl)silane $(n\text{-}C_3H_7)_2CH_3SiCH_2CH_2CH_2SCN$. A mixture of 150 ml of alcohol, 9.5 g of NaSCN, and 21.4 g of (3-chloropropyl)methyldipropylsilane [1] was boiled for 52 hours. The usual treatment gave 17.8 g (75%) of methyldipropyl(3-thiocyanatopropyl)silane, b.p. 116-118° (1 mm).

Found %: C 57.60, 57.77; H 10.06, 10.17; S 14.33, 14.28; Si 12.50, 12.50. $C_{11}H_{23}SiSN$.

Calculated %: C 57.57; H 10.11; S 13.97; Si 12.11.

Diethylmethyl(2-methyl-3-thiocyanatopropyl)silane $(C_2H_5)_2CH_3SiCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2SCN$. A mixture of 150 ml of ethanol, 17.2 g of NaSCN, and 37.5 g of (3-chloro-2-methylpropyl)diethylmethylsilane was boiled for 83 hours. The usual treatment gave 14.8 g (35.3%) of diethylmethyl(2-methyl-3-thiocyanatopropyl)silane, b.p. 82-87° (1.5 mm).

Found %: C 55.97, 56.03; H 9.84, 9.72; S 15.25, 15.18; Si 12.94, 13.21. $C_{10}H_{21}SiSN$.

Calculated %: C 55.75; H 9.82; S 14.88; Si 13.03.

Reaction of NaSCN with a mixture of (chloromethyl)trimethylsilane and (3-chloropropyl)trimethylsilane. To a solution of 24.3 g (0.3 mole) of NaSCN in 230 ml of ethanol, 36.78 g (0.3 mole) of $(CH_3)_3SiCH_2Cl$ and 45.2 g (0.3 mole) of $(CH_3)_3SiCH_2CH_2CH_2Cl$ [1] were added. The mixture was boiled for 16.5 hours with a break overnight. After the usual treatment, the product was distilled: none of the original α-chloro compound was isolated, but 13 g of the γ-chloro compound was recovered unchanged. The yield of trimethyl(thiocyanatomethyl)silane [8], b.p. 46° (1 mm) and n_D^{20} 1.4680, was 32.1 g (73.6%), but only 7 g (13.5%) of trimethyl(3-thiocyanatopropyl)silane [4], b.p. 70° (1 mm) and n_D^{20} 1.4690, was isolated.

Reaction of potassium acetate with a mixture of (chloromethyl)trimethylsilane and (3-chloropropyl)-trimethylsilane. A mixture of 100 ml of glacial acetic acid, 36.6 g (0.3 mole) of $(CH_3)_3SiCH_2Cl$, 45.2 g (0.3 mole) of (3-chloropropyl)trimethylsilane, and 29.4 g (0.3 mole) of $KOOCCH_3$ was heated in an autoclave at 200° for nine hours with a break overnight. After washing the product with water and drying it with calcium chloride, we distilled it through a column and obtained 16 g (0.13 mole) of the original α-chloro compound and 11 g (0.07 mole) of the γ-chloro compound. We obtained 14.5 g (0.1 mole, 33.4%) of $(CH_3)_3SiCH_2O_2CCH_3$ [8], b.p. 136-137°, and 25 g (0.14 mole, 48 %) of $(CH_3)_3SiCH_2CH_2CH_2O_2CCH_3$, b.p. 180-184°.

Found %: C 54.80, 54.81; H 10.32, 10.44; Si 16.02, 16.02. $C_8H_{18}SiO_2$.

Calculated %: C 55.12; H 10.41; Si 16.10.

2-Methyl-3-(trimethylsilyl)propanol acetic ester $CH_3\overset{\displaystyle O}{\overset{\|}{C}}OCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2Si(CH_3)_3$. A mixture of 65.6 g of (3-chloro-2-methylpropyl)trimethylsilane, 43 g of potassium acetate, and 150 ml of glacial acetic acid was heated for seven hours at 190° in an autoclave. The usual distillation gave 25.8 g (34.5%) of 2-methyl-3-(trimethylsilyl)propanol acetic ester, b.p. 70-75° (12 mm).

Found %: C 57.20, 57.35; H 10.63, 10.79; Si 14.77, 14.61. $C_9H_{20}SiO_2$.

Calculated %: C 57.40; H 10.70; Si 14.90.

(3-Ethoxypropyl)trimethylsilane $C_2H_5OCH_2CH_2CH_2Si(CH_3)_3$. A. Sodium (5 g) was dissolved in 90 ml of absolute ethanol, and 30 g of (3-chloropropyl)trimethylsilane [1] was added. The mixture was boiled for 20 hours with a break overnight. Salt was filtered off; it was dissolved in the water with which the filtrate was washed. Two distillations over sodium gave 22.6 g (71%) of (3-ethoxypropyl)trimethylsilane, b.p. 155-156°.

B. Potassium hydroxide (9 g) was dissolved in 34 g of ethanol, and 16 g of (3-chloropropyl)trimethylsilane was added. The mixture was heated at 160° in an autoclave for ten hours. The product was washed with water and dried with calcium chloride. Two distillations over sodium gave 12.5 g (73.5%) of (3-ethoxypropyl)trimethylsilane, b.p. 157-159°.

Found %: C 60.10, 59.91; H 12.60, 12.67; Si 17.20, 17.70; $C_8H_{20}SiO$.

Calculated %: C 59.93; H 12.57; Si 17.50.

Trimethyl(3-methoxy-2-methylpropyl)silane $(CH_3)_3SiCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2OCH_3$. A mixture of 19.7 g of (3-chloro-2-methylpropyl)trimethylsilane, 9 g of potassium hydroxide, and 22 ml of methanol was heated at 200° for four hours; the product was washed with water. Two distillations over sodium gave 9.5 g (48.2%) of trimethyl(3-methoxy-2-methylpropyl)silane, b.p. 149-152°.

Found %: C 59.88, 59.95; H 12.33, 12.41; Si 17.53, 17.46. $C_8H_{20}SiO$.

Calculated %: C 59.92; H 12.57; Si 17.52.

Reaction of potassium hydroxide with a mixture of (1-chloroethyl)trimethylsilane and (3-chloropropyl)trimethylsilane. A mixture of 28 g of $(CH_3)_3SiCHClCH_3$, 30 g of $(CH_3)_3SiCH_2CH_2CH_2Cl$, 23 g of potassium hydroxide, and 40 ml of methanol was heated for ten hours at 150°. The contents of the autoclave were then washed with water, and the organic layer was dried with calcium chloride and distilled through a column. We obtained 14 g (49%) of $(CH_3)_3SiCH=CH_2$, b.p. 54.5° and n_D^{20} 1.3852, and 17.2 g (60%) of (3-methoxypropyl)trimethylsilane, b.p. 140-141°.

Found %: C 57.40, 57.30; H 12.30, 12.30; Si 19.40, 19.20. $C_7H_{18}SiO$.

Calculated %: C 57.46; H 12.40; Si 19.19.

Pyrolysis of $(CH_3)_3SiCH_2CH_2CH_2O_2CCH_3$. In the course of two hours, 31.5 g of 3(trimethylsilyl)-propanol acetic ester was passed through a glass tube (working part 200 mm long and 1.5 mm in diameter) at 500°. The condensate was washed with sodium carbonate solution and dried with calcium chloride. Distillation over sodium gave 14 g (75.6%) of allyltrimethylsilane [12], b.p. 84-86°, n_D^{20} 1.4072, and d_4^{20} 0.7201. The flask contained 3.2 g of heavy residue. In the Raman spectrum analysis of the $(CH_3)_3SiCH_2CH=CH_2$ obtained, not even traces of $(CH_3)_3SiCH=CHCH_3$ or other compounds could be detected.

Pyrolysis of $CH_3Cl_2SiCH_2CH(CH_3)CH_2Cl$. In the course of six hours, 165.6 g of dichloro(3-chloro-2-methylpropyl)methylsilane was passed through a tube filled with active charcoal at 500°. Distillation of the condensate through a column gave 20 g of CH_3SiCl_3 and 31 g of the original $CH_3Cl_2SiCH_2CH(CH_3)CH_2Cl$. We obtained also 69 g (51%) of a fraction of b.p. 145-150°. Methylation of this fraction (CH_3MgCl was prepared from 20 g of magnesium in 300 ml of ether; boiling was continued for five hours) gave 21.3 g (40.7%) of a substance of b.p. 112-112.2° (742 mm); n_D^{20} 1.4200; d_D^{20} 0.7415; found MR 43.90; calculated MR 43.70; calculated 40.7%. Raman spectrum analysis of this substance showed that it was a mixture of

$$(CH_3)_3SiC\underset{\displaystyle C}{\underset{|}{C}}=C,\quad (CH_3)_3SiC=\underset{\displaystyle C}{\underset{|}{C}}C,\text{ and }(CH_3)_3SiCC=CC.$$

N,N-Diethyl-3-(trimethylsilyl)propylamine $(CH_3)_3SiCH_2CH_2CH_2N(C_2H_5)_2$. A mixture of 15 g of (3-chloropropyl)trimethylsilane [1] and 19 g of diethylamine was heated for five hours at 160° in a 75-ml autoclave. On the next day the contents of the autoclave were washed with water rendered alkaline with

sodium hydroxide, and the organic layer was dried with sodium sulfate. Distillation through a column gave 6.5 g of the original $(CH_3)_3SiCH_2CH_2CH_2Cl$ and 6 g (56.7%) of N,N-diethyl-3-(trimethylsilyl)propylamine, b.p. 192-193°.

Found %: C 63.70, 63.75; H 13.16, 13.32; Si 15.20, 14.96. $C_{10}H_{25}SiN$.

Calculated %: C 64.09; H 13.44; Si 14.97.

Triethyl[3-(trimethylsilyl)propyl]ammonium iodide $(CH_3)_3SiCH_2CH_2CH_2N(C_2H_5)_3\ I^-$. Ethyl iodide (6 g) was added to a solution of 5 g of $(CH_3)_3SiCH_2CH_2CH_2N(C_2H_5)_2$ in 30 ml of ether. After four days the precipitate of the salt was filtered off and washed with ether: 0.8 g (8.7%). After seven days the total yield had reached 14.2%, and after 13 days it was 21.8%; m.p. 125-127°.

Found %: C 41.90, 42.00; H 8.96, 8.91; Si 8.12, 8.57; I 37.00; 36.74. $C_{12}H_{30}SiNI$.

Calculated %: C 41.97; H 8.80; Si 8.17; I 36.97.

2-Methyl-3-(trimethylsilyl)propanol $(CH_3)_3SiCH_2\underset{\displaystyle CH_2}{\underset{|}{C}}HCH_2OH$. Methanol (20 g) and three drops of concentrated sulfuric acid were added to 25.3 g of 2-methyl-3-(trimethylsilyl)propanol acetic ester. After three days methyl acetate was distilled from the mixture and fresh methanol and two more drops of sulfuric acid were added. After three more days vacuum distillation gave 15 g (76.3%) of 2-methyl-3-(trimethylsilyl)propanol, b.p. 73.5° (12 mm).

Found %: C 57.12, 57.01; H 12.28, 12.45; Si 18.87, 18.70. $C_7H_{18}SiO$.

Calculated %: C 57.46; H 12.40; Si 19.19.

3-[2-Methyl-3-(trimethylsilyl)propoxy]propionitrile $(CH_3)_3SiCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2OCH_2CH_2CN$. Two drops of sodium methoxide solution were added to 14.6 g of $(CH_3)_3SiCH_2CH(CH_3)CH_2OH$, and 8 g of acrylonitrile was then added slowly. After one day the liquid was washed with acidified water, dried with calcium chloride, and fractionated. The yield of $(CH_3)_3SiCH_2CH(CH_3)CH_2OCH_2CH_2CN$, b.p. 97-100°, was 20 g (79.5%).

Found %: C 60.30, 60.20; H 10.70, 10.58; Si 13.90, 13.75. $C_{10}H_{21}SiNO$.

Calculated %: C 60.24; H 10.61; Si 14.08.

Reaction of trimethyl(thiocyanatomethyl)silane with sulfuric acid. Trimethyl(thiocyanatomethyl) silane (20.5 g) was added to 21 ml of concentrated sulfuric acid cooled to 0°. The contents of the flask were kept overnight under ice cooling and were then kept for 24 hours at room temperature. The liquid, which had formed into layers, was poured onto ice. The crystals that formed after two hours were washed with water and dried over calcium chloride. The product, amounting to 11 g, consisted of yellow crystals, which became pure white when washed with dry ether. They melted with decomposition at 130°.

Found %: C 24.35, 24.46; H 6.87, 6.91; S 26.25, 26.11; Si 12.44, 12.66. $C_5H_{13}SiSNO$.

Calculated %: C 36.77; H 8.00; S 19.63; Si 17.18.

SUMMARY

1. It was confirmed that in nucleophilic bimolecular substitution reactions (reaction with NaSCN) the C — Cl bond in compounds of formula $(CH_3)_3Si(CH_2)_nCl$ is more reactive when in the α-position than when in the γ-position. However, in reactions with potassium acetate the mobility of γ-halogen was found to be higher than that of α-halogen. It is suggested that this reaction has a different mechanism.

2. It was shown that organosilicon amines having a γ-amino group are less reactive toward C_2H_5I than those in which the amino group is in the α-position.

3. It was found that γ-chloro organosilicon compounds do not lose HCl when treated with quinoline or alcoholic alkali. In the latter case ethers are formed.

4. It was found that pyrolysis of $(CH_3)_3SiCH_2CH_2CH_2O_2CCH_3$ gives only allyltrimethylsilane, but pyrolisis of $CH_3Cl_2SiCH_2CH(CH_3)CH_2Cl$ gives a mixture of alkenylsilanes with some isomerization of the molecular skeleton.

5. Sixteen compounds were synthesized for the first time; these contained Cl, SCN, $OOCCH_3$, OR, and OH groups in the γ-position with respect to silicon.

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ADDITION OF SILANES CONTAINING SILICON-ATTACHED HYDROGEN TO UNSATURATED COMPOUNDS IN PRESENCE OF PLATINIZED CHARCOAL

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Peroxides, ultraviolet radiation, and halides of aluminum, zinc, and boron were, until recently, almost the only known initiators for the additions of silanes containing silicon-attached hydrogen to unsaturated compounds:

$$\equiv Si - H + CH_2 = CHR \rightarrow \equiv SiCH_2CH_2R.$$

In the investigations of Wagner [1] and of Bailey and Pines [2] it was found for the first time that platinized charcoal can also act as a good catalyst for this reaction. The discovery of the use of platinized charcoal prompted the search for other heterogeneous catalysts for this reaction [3], which is of practical importance. At the same time there arose another question of no less interest: the effect of the structures of the original silanes and unsaturated compounds on the course of the addition reaction on a given heterogeneous catalyst. In the two preceding communications [4,5] we were only partly concerned with this matter. In the present investigation we had the object of studying the addition reaction from the point of view of the specific action of platinized charcoal, considered in its relation to the action of peroxides.

It is known that, in the case of peroxides, the structure of the original silane has a substantial effect on the yield of addition products. The silanes that add most readily to unsaturated compounds in presence of peroxides are those containing electronegative groups, such as Cl_3SiH and $(C_6H_5)_3SiH$. The replacement of chlorine in Cl_3SiH by an aliphatic radical and increase in the complexity of the structure of this radical generally result in a reduction in the yield of addition product. Thus, according to Burkhard and Krieble [6], Cl_3SiH reacts with 1-pentene and gives a 44% yield of addition product, but CH_3SiHCl_2, reacting with the same compound, gives only 10% of dichloromethylpentylsilane; methyldipropylsilane $CH_3SiH(C_3H_7)_2$ reacts still less readily [6]. The part played by the structure of the unsaturated compound is of no less importance. Addition products are formed in high yield only when, under the conditions of reaction in presence of peroxides, the unsaturated compound does not readily undergo the polymerization side reaction and when the double bond of this compound is not too greatly screened by substituents capable of creating steric hindrance [6,7].

The addition reaction in presence of platinized charcoal differs from reaction in presence of peroxides in being a heterogeneous catalytic process. It is to be expected, therefore, that under these conditions the structures of the reactants (silane and unsaturated compound) will have different effects on the course of the addition reaction.

1. Investigation of the Effect of the Structure of the Silane. For investigation we selected a series of silanes containing silicon-attached hydrogen and having a gradually diminishing number of chlorine atoms attached to silicon: Cl_3SiH, CH_3SiHCl_2, $C_2H_5SiHCl_2$, i-$C_3H_7SiHCl_2$, n-$C_4H_9SiHCl_2$, $(C_2H_5)(CH_3)SiHCl$, $(C_2H_5)_2SiHCl$, $(C_2H_5)_2(CH_3)SiH$. The unsaturated compounds used were allyl chloride and allyltrichlorosilane. The reaction conditions were approximately constant (see Tables 1 and 2). Table 1 shows clearly that silanes of the types $RSiHCl_2$ and R_2SiHCl (CH_3SiHCl_2, $C_2H_5SiHCl_2$, and $CH_3(C_2H_5)SiHCl$) add most readily to allyl chloride. In spite of the results of Bailey and Pines [2], under our conditions trichlorosilane

TABLE 1

$\equiv Si - H + CH_2 = CHCH_2Cl \rightarrow \equiv SiCH_2CH_2CH_2Cl$

Experiment No.	Original silane	Amount, g (moles)	Amount of $CH_2=CHCH_2Cl$ g (moles)	Amount of 1% Pt on C (g)	Reaction temperature (°C)	Duration of heating (hrs)	Maximum excess pressure (atm)	Reaction product	Amount (g)	Yield * (%)
1	Cl_3SiH	135 (1)	76.5 (1)	0.3	160	6	7	$CH_2(Cl)_2SiCH_2CH_2CH_2Cl$	—	0 (0)
2	$Cl_2SiH(CH_3)$	115 (1)	76.5 (1)	0.3	160	6	12	$C_2H_5(Cl)_2SiCH_2CH_2CH_2Cl$	92	48.0 (50.0)
3	$Cl_2SiH(C_2H_5)$	129 (1)	76.5 (1)	0.3	160	6	12	$i\text{-}C_3H_7(Cl)_2SiCH_2CH_2CH_2Cl$	100	48.8 (48.8)
4	$Cl_2SiH(i\text{-}C_3H_7)$	41 (0.29)	22 (0.29)	0.2	160	9	8	$C_4H_9(Cl)_2SiCH_2CH_2CH_2Cl$	16	26.0 (29.5)
5	$Cl_2SiH(n\text{-}C_4H_9)$	50 (0.32)	24 (0.32)	0.2	160	6	—	$(CH_3)(C_2H_5)ClSiCH_2CH_2CH_2Cl$	22	30.0 (31.0)
6	$ClSiH(CH_3)(C_2H_5)$	86 (0.8)	61 (0.8)	0.3	160	7	9	$(C_2H_5)_2ClSiCH_2CH_2CH_2Cl$	59.5	40.5 (40.5)
7	$ClSiH(C_2H_5)_2$	30.5 (0.25)	19 (0.25)	0.1	180	6	17	$(CH_3)(C_2H_5)_2SiCH_2CH_2CH_2Cl$	10.3	21.0 (21.0)
8	$HSi(CH_3)(C_2H_5)_2$	63 (0.62)	47 (0.62)	0.3	160	6	—	$(CH_3)(C_2H_5)_2SiCH_2CH_2CH_2Cl$	2	1.8 (1.8)

* The figure in parentheses is the per cent yield on the amount of silane that reacted.

does not add to allyl chloride; also, replacement of silicon-attached hydrogen by chlorine, always observed in the case of other silanes containing silicon-attached hydrogen, does not occur. $(C_2H_5)_2CH_3SiH$ added to allyl chloride with great difficulty, and more than one-half of the original silane underwent neither the addition reaction nor the reaction of replacement of silicon-attached hydrogen by chlorine. In the case of silanes of the type $RSiHCl_2$, increase in the complexity of the radical ($R \equiv i\text{-}C_3H_7$, $n\text{-}C_4H_9$) also results in reduction in yield of addition products (see Experiments 4 and 5).

When the data in Table 2 on the addition of silanes to allyltrichlorosilane are analyzed, it can again be seen that the highest yield of addition products is given by the same silanes of the types $RSiHCl_2$ and R_2SiHCl (see Experiments 10 and 11). It is true that in this case the picture is not so clear. Also, trichlorosilane, which did not add to allyl chloride, reacted with allyltrichlorosilane to give 1,1,1,5,5,5-hexachloro-1,5-disilapentane in a fairly high yield (Experiment 9).

The above-noted difference in the readiness with which Cl_3SiH, on the one hand, and CH_3SiHCl_2 and $C_2H_5SiHCl_2$ on the other, undergo addition is observed also when butadiene is used (see Experiments 19 and 20). In this case also, unlike Bailey and Pines [2], we did not succeed in effecting the addition of Cl_3SiH to butadiene. Comparison of all these results with those obtained by the use of peroxides indicates that, whereas in the case of peroxides the most suitable silanes for the synthesis are of the type X_3SiH ($X = Cl$, C_6H_5), in the case of platinized charcoal the most suitable silanes are of the types $RSiHCl_2$ and R_2SiHCl.

2. Investigation of the Effect of the Structure of the Unsaturated Compound. In this case the silanes used were of the type $RSiHCl_2$, i.e. dichloromethyl- and dichloroethyl-silanes. The olefins used, the reaction conditions, and the yields of addition products are stated in Table 3. It will be readily seen that unsaturated compounds having substituents that screen the double bond (Cl, F) give lower yields of addition products in spite of more severe conditions of reaction. The use of compounds with "active" double bonds ($Cl_3SiCH_2CH = CH_2$, $CH_2 = CH - CH = CH_2$, $CH_2 = CHCH_2Cl$, $CH_2 = C(CH_3) - CH_2Cl$, and others, Experiments 2, 3, 10, 19, 20, and 21) results in considerable increase in the yields of addition products. It is interesting that, in the case of allyltrichlorosilane (Experiment 10), in spite of milder reaction conditions, the yield is considerably higher than in the case of allyltrimethylsilane (Experiment 18) (64%, as against 35%).

In a previous communication [5] we discussed the addition of CH_3SiHCl_2 and $C_2H_5SiHCl_2$ to tetrafluoroethylene and to chlorotrifluoroethylene in detail. In

TABLE 2

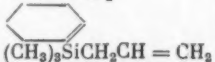
$\equiv Si - H + CH_2 = CHCH_2SiCl_3 \rightarrow \equiv SiCH_2CH_2CH_2SiCl_3$

Experiment No.	Original silane	Amount, g (moles)	Amount of unsaturated compound, g (moles)	Amount of 1% Pt on C (g)	Reaction temperature (°C)	Duration of heating (hrs)	Maximum excess pressure (atm)	Reaction product	Amount (g)	Yield* (%)
9	Cl_3SiH	23.2 (0.17)	30 (0.17)	0.2	170	7	18.3	$Cl_3SiCH_2CH_2CH_2SiCl_3$	26.5	50.0 (68.0)
10	$Cl_2SiH(CH_3)$	13.1 (0.12)	20 (0.12)	0.2	170	6	9.5	$Cl_3SiCH_2CH_2CH_2Si(Cl)_2(CH_3)$	21.1	64.0 (82)
11	$ClSiH(C_2H_5)_2$	21 (0.17)	30 (0.17)	0.2	170	2	8.5	$Cl_3SiCH_2CH_2CH_2Si(Cl)(C_2H_5)_2$	24.6	48.5 (50.0)
12	$HSi(CH_3)(C_2H_5)_2$	14.6 (0.14)	25 (0.14)	0.2	170	4,5	11	$Cl_3SiCH_2CH_2CH_2Si(CH_3)(C_2H_5)_2$	13.4	33.8 (54.5)

*The figure in parentheses is the per cent yield on the amount of silane that reacted.

TABLE 3

$RSiHCl_2 + \rangle C = C \langle \rightarrow RSi(Cl)_2\overset{|}{C}-\overset{|}{C}-H$

Experiment No.	Original olefin	Amount, g (moles)	Amount of silane, g (moles)	Amount of 1% Pt on C (g)	Reaction temperature (°C)	Duration of heating (hrs)	Maximum excess pressure (atm)	Reaction product	Amount (g)	Yield* (%)
13	$Cl_2C = CHCl$	132 (1.0)	115 (1.0)	0.3	160	7	—	—	—	0 (0)
14	$CH_2 = CHCl$	108 (1.71)	102 (0.89)	0.5	160	6	30	$CH_3(Cl)_2SiCHClCH_3$	12	7.6 (10.4)
15	$CF_2 = CF_2$	—	115 (1.0)	0.3	160	17	—	$CH_3(Cl)_2SiCF_2CHF_2$	13.9	(14)
16	$CClF = CF_2$	110 (0.95)	115 (1.0)	0.3	160	15	30	$CH_3(Cl)_2SiCClFCHF_2$	10	4.5 (23)
17		60.5 (0.74)	85 (0.74)	0.3	220	16	—	$CH_3(Cl)_2Si$	8.7	6.0 (20.7)
18	$(CH_3)_3SiCH_2CH = CH_2$	25.2 (0.22)	25 (0.22)	0.1	170	8	14	$(CH_3)_3SiCH_2CH_2CH_2Si(Cl)_2CH_3$	17.3	34.5 (61.8)
19	$CH_2 = CH - CH = CH_2$	75 (1.4)	115 (1.0)	0.3	160	10	—	$CH_3(Cl)_2SiC_4H_7$	25.2	14.9 (33.2)
20	$CH_2 = CH - CH = CH_2$	108 (2.0)	129 (1.0)**	0.3	160	10	—	$C_2H_5(Cl)_2SiC_4H_7$	77	42.1 (51.7)
21	$CH_2 = C(CH_3) - CH_2Cl$	90.5 (1.0)	115 (1.0)	0.5	160	6	31	$CH_3(Cl)_2SiCH_2CH(CH_3)CH_2Cl$	120	58.0 (75.5)
22	$CH_2 = CH -$	51 (0.47)	61 (0.47)**	0.15	180	6	7.5	$C_2H_5(Cl)_2SiCH_2CH_2$	85	75.9 (81.0)

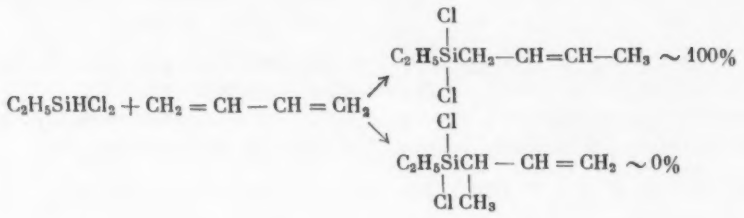
*The figure in parentheses is the per cent yield on the amount of silane that reacted.

**In this reaction the silane used was dichloroethylsilane $C_2H_5SiHCl_2$.

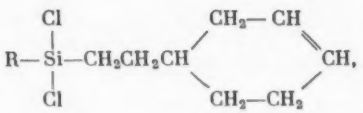
supplementation of this we may mention that in the reaction of CH_3SiHCl_2 with $F_2C = CF_2$, as well as the product of addition of one molecule of tetrafluoroethylene, we isolated also the compound $CH_3Si(Cl)_2CF_2$-$CF_2CF_2CF_2H$, which is derived from two $F_2C = CF_2$ molecules (Experiments 15 and 16). This indicates that in this case telomerization occurs*. The fractionation curves of the products of the addition of CH_3SiHCl_2 and $C_2H_5SiHCl_2$ to $F_2C = CF_2$ clearly indicate that some higher-boiling telomers are also formed, but we did not succeed in isolating them owing to the smallness of the amount formed.

In previous communications [4,5] we pointed out also the necessity of investigating the direction of the addition of the silane to the unsaturated compound in each concrete case. Thus, it was established that in the case of allyl and 2-methylallyl chlorides the silicon-attached hydrogen of the silane adds to the less-hydrogenated carbon atom and the residue $[R(Cl)_2Si]$ to the more hydrogenated carbon atom, whereas in the case of vinyl chloride addition occurs in the opposite direction. There was undoubted interest in the more detailed investigation of this matter for butadiene, allyltrichlorosilane, and other unsaturated compounds.

Investigation of the products of addition of $C_2H_5SiHCl_2$ to butadiene with the aid of Raman spectra showed that only 1,4-addition occurs (Experiment 20):



We must discuss the addition reaction between $RSiHCl_2$ and butadiene in greater detail. Unlike Bailey and Pines [2], we carried out the addition of Cl_3SiH, CH_3SiHCl_2, and $C_2H_5SiHCl_2$ in such a way that all the butadiene was introduced into the autoclave in one portion, and not gradually as the reaction progressed. It was not by chance, therefore, that we always observed the formation of the butadiene dimer, 4-vinylcyclohexene $CH_2 = CH$– . This compound, which is fairly reactive, reacts in turn with CH_3SiHCl_2 or $C_2H_5SiHCl_2$. We confirmed this in a special experiment (see Experiment 22). The products evidently have the following structure:



in which $R = CH_3$, C_2H_5.

In the addition of Cl_3SiH to allyltrichlorosilane, two products may be formed:

(I) $Cl_3SiCH_2CH_2CH_2SiCl_3$; (II) $Cl_3SiCH_2CHSiCl_3$ with CH_3 on the CH group

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*When the present work was complete and had been partially published [5], papers on the telomerization of silanes containing silicon-attached hydrogen with $F_2C = CF_2$ [10] and $CH_2 = CH_2$ [11] appeared.

Compound (II) was prepared by Petrov and Smetankina [8] by direct synthesis from 1,2-dichloropropane. Our addition product differed greatly from (II) in its constants, and it was therefore undoubtedly compound (I). Comparison of physical properties indicates that other silanes add to $Cl_3SiCH_2CH=CH_2$ and $(CH_3)_3SiCH_2CH=CH_2$ in the same way.

In conclusion we will point out two interesting facts noted in the course of this work.

1. In the preparation of $(C_2H_5)(CH_3)SiHCl$ and of $(C_2H_5)_2SiHCl$ from CH_3SiHCl_2 and $C_2H_5SiHCl_2$, respectively, and C_2H_5MgBr, we obtained also considerable amounts of $(C_2H_5)(CH_3)SiHBr$ and $(C_2H_5)_2SiHBr$, formed evidently from the chloro compounds and MgClBr (Experiments 23 and 24).

2. In reaction with magnesium, γ-chloro compounds having at least one silicon-attached chlorine may form a four-membered rind containing silicon (Experiments 25-27), as also does (3-bromopropyl)-chlorodimethylsilane [9].

EXPERIMENTAL

The addition of silanes to olefins was carried out in some cases in a 500-ml rotating autoclave and in others in a 200-ml stainless steel bomb at 160-170°. The principal results and the experimental conditions are presented in Tables 1, 2, and 3. More detailed data on the reaction products are given in the text.

1. Attempt to prepare trichloro(3-chloropropyl)silane $Cl_3SiCH_2CH_2CH_2Cl$. When the autoclave was opened, a small amount of gas was liberated. The weight of crude product was 196 g. In the fractionation through a column the product began to decompose at 130°. The residue was vacuum-fractionated twice. No trichloro(3-chloropropyl)silane was obtained. The substances isolated were:

1) trichlorosilane (92 g); b.p. 31° (751 mm);

2) allyl chloride (47 g); b.p. 44.5° (751 mm).

2. Dichloro(3-chloropropyl)methylsilane $CH_3(Cl)_2SiCH_2CH_2CH_2Cl$. The weight of crude product was 173 g. Fractionation through a column of 35 theoretical plates gave:

1) a mixture of allyl chloride and dichloromethylsilane (10 g), b.p. 43° (754 mm);

2) trichloromethylsilane (30 g), b.p. 66° (754 mm);

3) dichloromethylpropylsilane (18.6 g), b.p. 124.4° (754 mm); d_4^{20} 1.0383; n_D^{20} 1.4250;

4) dichloro(3-chloropropyl)methylsilane (92 g), b.p. 184.5° (754 mm), d_4^{20} 1.2045, n_D^{20} 1.4580.

3. Dichloro(3-chloropropyl)ethylsilane $C_2H_5(Cl_2)SiCH_2CH_2CH_2Cl$. The weight of crude product was 199 g. Fractionation through a 35-plate column gave:

1) unchanged allyl chloride (7.5 g), b.p. 44.0° (738 mm);

2) trichloroethylsilane (43.5 g), b.p. 99° (738 mm);

3) dichloroethylpropylsilane (18.6 g), b.p. 150° (738 mm); d_4^{20} 1.0343; n_D^{20} 1.4370;

4) dichloro(3-chloropropyl)ethylsilane (100.0 g), b.p. 206° (738 mm), d_4^{20} 1.1809, n_D^{20} 1.4661.

4. Dichloro(3-chloropropyl)isopropylsilane $(CH_3)_2CH(Cl)_2SiCH_2CH_2CH_2Cl$. Fractionation through a 35-plate column of 56 g of reaction products gave:

1) trichloroisopropylsilane (7 g), b.p. 119.5° (769 mm);

2) residue (22 g) boiling above 210° (759 mm); vacuum fractionation of this gave 16 g of dichloro(3-chloropropyl)isopropylsilane, b.p. 55-56° (3 mm), d_4^{20} 1.1512, n_D^{20} 1.4685, found MR 53.07, calculated MR 52.90.

Found %: H 6.17, 5.98; C 33.34, 33.56; Cl 47.48, 47.59; Si 12.71, 12.57. $C_6H_{13}SiCl_3$.

Calculated %: H 5.97; C 32.81; Cl 48.44; Si 12.78.

5. Butyldichloro(3-chloropropyl)silane $CH_3CH_2CH_2CH_2(Cl)_2SiCH_2CH_2CH_2Cl$. The weight of crude product was 72 g. Fractionation through a 35-plate column gave:

1) butyltrichlorosilane (17 g), b.p. 145.5° (746 mm);

2) residue (36 g) boiling above 190° (746 mm); two vacuum fractionations gave 22 g of butyldichloro(3-chloropropyl)silane, b.p. 74° (3 mm), d_4^{20} 1.1276, n_D^{20} 1.4682, found MR 57.61, calculated MR 57.03.

Found %: H 6.51, 6.58; C 36.18, 36.23; Cl 45.14, 45.22; Si 12.04, 11.88. $C_7H_{15}SiCl_3$.

Calculated %: H 6.47; C 35.99; Cl 45.53; Si 12.01.

6. Chloro(3-chloropropyl)ethylmethylsilane $(CH)_3(C_2H_5)ClSiCH_2CH_2CH_2Cl$. The weight of crude reaction products was 143 g. Fractionation through a 35-plate column gave:

1) dichloroethylmethylsilane (30 g), b.p. 101° (756 mm);

2) chloroethylmethylpropylsilane (12.4 g), b.p. 141° (759 mm), d_4^{20} 0.8825, n_D^{20} 1.4266, found MR 43.80, calculated MR 43.80.

Found %: H 10.10, 9.94; C 48.04, 48.07; Cl 23.55; Si 18.61, 18.60. $C_6H_{15}SiCl$.

Calculated %: H 10.03; C 47.82; Cl 23.53; Si 18.62.

3) chloro(3-chloropropyl)ethylmethylsilane (59.5 g), b.p. 197.4° (759 mm), d_4^{20} 1.0333, n_D^{20} 1.4559, found MR 48.70, calculated MR 48.64.

Found %: H 7.66, 7.66; C 39.16, 39.25; Cl 37.85, 38.25; Si 14.83, 14.94. $C_6H_{14}SiCl_2$.

Calculated %: H 7.62; C 38.92; Cl 38.30; Si 15.16.

7. Chloro(3-chloropropyl)diethylsilane $(C_2H_5)_2ClSiCH_2CH_2CH_2Cl$. The weight of the crude mixture of reaction products was 40 g. Fractionation through a 35-plate column gave:

1) dichlorodiethylsilane (13.2 g), b.p. 129° (744 mm);

2) chlorodiethylpropylsilane (3.6 g), b.p. 164.6° (744 mm), d_4^{20} 0.9047, n_D^{20} 1.4377;

3) chloro(3-chloropropyl)diethylsilane (10.3 g), b.p. 218.5° (744 mm), d_4^{20} 1.0331, n_D^{20} 1.4614, found MR 53.04, calculated MR 53.03.

Found %: H 8.18, 8.27; C 42.10, 42.07; Cl 35.50, 35.95; Si 14.23, 13.83. $C_7H_{16}SiCl_2$.

Calculated %: H 8.09; C 42.31; Cl 35.54; Si 14.06.

8. (3-Chloropropyl)diethylmethylsilane $(CH_3)(C_2H_5)_2SiCH_2CH_2CH_2Cl$. The weight of the crude mixture of reaction products was 102 g. Fractionation through a 35-plate column gave:

1) allyl chloride (19.6 g), b.p. 44.5° (753 mm);

2) diethylmethylsilane (35 g), b.p. 77.6° (753 mm);

3) chlorodiethylmethylsilane (14 g), b.p. 119-120° (753 mm);

4) residue (16 g); two vacuum distillations gave 2 g of (3-chloropropyl)diethylmethylsilane*, b.p. 55-56° (3 mm), d_4^{20} 0.8957, n_D^{20} 1.4482, found MR 53.73, calculated MR 53.40.

9. 1,1,1,5,5,5-Hexachloro-1,5-disilapentane $Cl_3SiCH_2CH_2CH_2SiCl_3$. The weight of the crude mixture of reaction products was 50 g. Fractionation through a 35-plate column gave 26.5 g of 1,1,1,5,5,5-hexachloro-1,5-disilapentane, b.p. 228° (748 mm), d_4^{20} 1.4394, n_D^{20} 1.4732, found MR 60.62, calculated MR 60.84.

Found %: H 1.75, 1.77; C 11.60, 11.55; Cl 67.74, 67.84; Si 18.63, 18.73. $C_3H_6Si_2Cl_6$.

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*The analytical results on this compound indicated that it was not adequately pure.

Calculated %: H 1.94; C 11.59; Cl 68.42; Si 18.05.

10. 1,1,1,5,5-Pentachloro-5-methyl-1,5-disilapentane $Cl_3SiCH_2CH_2CH_2Si(Cl)_2(CH_3)$. Fractionation of the crude mixture of reaction products (30 g) through a 35-plate column gave 21.1 g of 1,1,1,5,5--pentachloro-5-methyl-1,5-disilapentane, b.p. 230° (741 mm); d_4^{20} 1.1758, n_D^{20} 1.4704, found MR 61.36, calculated MR 61.21.

Found %: H 3.29, 3.10; C 16.75, 16.76; Cl 61.30, 61.27; Si 19.28, 19.18. $C_4H_9Si_2Cl_5$.

Calculated %: H 3.12; C 16.54; Cl 61.02; Si 19.32.

11. 1,1,1,5-Tetrachloro-5,5-diethyl-1,5-disilapentane $Cl_3SiCH_2CH_2CH_2Si(Cl)(C_2H_5)_2$. Fractionation of the crude mixture of reaction products (50 g) through a 35-plate column gave 24.6 g of 1,1,1,5--tetrachloro-5,5-diethyl-1,5-disilapentane, b.p. 258-259° (741 mm); d_4^{20} 1.1758, n_D^{20} 1.4680, found MR 70.49, calculated MR 70.60.

Found %: H 5.50, 5.45; C 28.47, 28.57; Cl 45.90, 46.87; Si 19.25, 19.09. $C_7H_{16}SiCl_4$.

Calculated %: H 5.41; C 28.20; Cl 47.57; Si 18.82.

12. 1,1,1-Trichloro-5,5-diethyl-5-methyl-1,5-disilapentane $Cl_3SiCH_2CH_2CH_2Si(CH_3)(C_2H_5)_2$. The weight of the crude mixture of reaction products was 39 g. Fractionation through a 35-plate column gave:

1) diethylmethylsilane (5.6 g), b.p. 98° (749 mm);

2) 1,1,1-trichloro-5,5-diethyl-5-methyl-1,5-disilapentane, b.p. 242° (749 mm), d_4^{20} 1.0658, n_D^{20} 1.4593, found MR 71.28, calculated MR 70.97.

Found %: H 6.79, 6.78; C 34.64, 34.58; Cl 38.57, 38.43; Si 19.81, 20.46. $C_8H_{19}Si_2Cl_3$.

Calculated %: H 6.90; C 34.59; Cl 38.30; Si 20.21.

13 and 14. See Table 3 and the paper [5].

15 and 16. Addition of CH_3SiHCl_2 and $C_2H_5SiHCl_2$ to $F_2C=CF_2$ and to $CF_2=CFCl$. The details of these experiments and the properties of the addition products have been described by us previously [5]. Tetrafluoroethylene, unlike chlorotrifluoroethylene, was passed into the autoclave several times in the form of a gas at an initial pressure of 7-8 atm. In the case of CH_3SiHCl_2 heating at 160° was continued for 17 hours, and in the case of $C_2H_5SiHCl_2$ for 28 hours. In the first case the weight of crude reaction products was 104 g, and in the second case it was 145 g.

Fractionation of the products of the addition of CH_3SiHCl_2 to $CF_2=CF_2$ through a 35-plate column gave, apart from $CH_3Si(Cl)_2CF_2CF_2H$ [5], also 6.1 g of $CH_3Si(Cl)_2CF_2CF_2CF_2CF_2H$, b.p. 138° (753 mm), d_4^{20} 1.5119, n_D^{20} 1.3570.

17. Dichlorocyclohexylmethylsilane $(CH_3)(Cl)_2SiC_6H_{11}$. Fractionation of the reaction products through a column gave:

1) dichloromethylsilane (60.5 g), b.p. 41° (752 mm);

2) cyclohexene (51 g), b.p. 82.4° (752 mm);

3) dichlorocyclohexylmethylsilane (8.7 g), b.p. 201° (752 mm), d_4^{20} 1.0953, n_D^{20} 1.4724, found MR 50.44, calculated MR 50.56.

Found %: C 42.76, 42.55; H 7.24, 7.21; Cl 35.81; Si 14.64, 14.53. $C_7H_{14}SiCl_2$.

Calculated %: C 42.64; H 7.16; Cl 35.97; Si 14.23.

Attempts to add dichloromethylsilane to cyclohexene in presence of the same catalyst but at lower temperatures (160°) were unsuccessful.

18. 1,1-Dichloro-1,5,5,5-tetramethyl-1,5-disilapentane $(CH_3)_3SiCH_2CH_2CH_2Si(Cl)_2(CH_3)$. The weight of crude products was 43 g. Fractionation through a column gave:

1) dichloromethylsilane (11 g), b.p. 42° (751 mm);

2) allyltrimethylsilane (8.6 g), b.p. 85.6°;

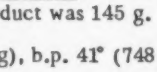
3) 1,1-dichloro-1,5,5,5-tetramethyl-1,5-disilapentane, b.p. 201° (751 mm); d_4^{20} 0.9730, n_D^{20} 1.4428, found MR 62.44, calculated MR 62.32.

Found %: C 36.41, 36.46; H 7.92, 7.82; Cl 30.84, 31.23; Si 24.79, 24.72. $C_7H_{18}Si_2Cl_2$.

Calculated %: C 36.67; H 7.92; Cl 30.93; Si 24.48.

19. Addition of CH_3Cl_2SiH to butadiene. When the autoclave was opened, a small amount of gas was liberated. The weight of crude product was 145 g. Fractionation through a column gave:

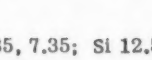
1) dichloromethylsilane (63 g), b.p. 41° (748 mm);

2) 4-vinylcyclohexene $CH_2 = CH$—  , (16.6 g), b.p. 128.5° (750 mm), d_4^{20} 0.8274, n_D^{20} 1.4649, found MR 36.14, calculated MR 36.10;

3) 2-butenyldichloromethylsilane (25.2 g), b.p. 147° (750 mm), d_4^{20} 1.0463, n_D^{20} 1.4519, found MR 43.50, calculated MR 42.96; the presence of $(CH_3)Cl_2SiCH_2CH = CHCH_3$ was confirmed by the fact that in the Raman spectrum of the diethylated product $(CH_3)(C_2H_5)_2SiC_4H_7$ only the characteristic frequencies of the grouping $\equiv SiCH_2—CH=CH—CH_3$ (1662 cm^{-1} and 1646 cm^{-1}) were observed *;

Found %: H 6.14, 6.05; C 36.94, 36.99; Si 16.49, 16.45. $C_5H_{10}SiCl_2$.

Calculated %: H 5.96; C 35.51; Si 16.59.

4) residue (40 g); vacuum distillation gave 10 g of dichloro(3-cyclohexen-1-ylethyl)methylsilane $(CH_3)(Cl)_2SiCH_2CH_2$  , b.p. 79.5-80.5° (3 mm), d_4^{20} 1.0771, n_D^{20} 1.4829, found MR 59.17, calculated MR 59.35.

Found %: C 48.65, 48.72; H 7.35, 7.35; Si 12.58, 12.46; Cl 31.74, 31.46. $C_9H_{16}SiCl_2$.

Calculated %: C 48.43; H 7.23; Si 12.57; Cl 31.77.

20. Addition of $C_2H_5SiHCl_2$ to butadiene. The weight of crude reaction products was 225 g. Fractionation through a column gave:

1) dichloroethylsilane (24 g), b.p. 74.5° (760 mm);

2) 4-vinylcyclohexene $CH_2 = CH$ (16.6 g), b.p. 128.5° (760 mm);

3) 2-butenyldichloroethylsilane (77 g), b.p. 171.5° (768 mm), d_4^{20} 1.0450, n_D^{20} 1.4566, found MR 47.69, calculated MR 47.47.

Found %: H 6.74, 6.67; C 39.36, 39.55; Cl 38.59, 38.50; Si 14.90, 14.93. $C_6H_{12}SiCl_2$.

Calculated %: H 6.61; C 39.35; Cl 38.72; Si 15.32.

The presence of 2-butenyldichloroethylsilane was proved as follows:

a) The product of the addition of dichloroethylsilane to butadiene was treated with C_2H_5MgBr in order to give $(C_2H_5)_3SiC_4H_7$, b. p. 183.8-188° (749 mm), d_4^{20} 0.7994, n_D^{20} 1.4485, found MR 57.10, calculated MR 57.23. The following frequencies were found in the Raman spectrum of this compound (I)*:

ν (cm^{-1}): 175 (1), 296 (3), 333 (1), 373 (1), 401 (1), 443 (3), 505 (0b), 543 (2), 566 (5b), 580 (2), 568 (1), 739 (1), 767 (4), 790 (2), 824 (1), 909 (3b), 972 (4b), 1017 (3b), 1121 (2b), 1158 (5b), 1191 (0), 1238 (3), 1265 (4), 1308 (3b), 1366 (1), 1380 (1), 1420 (4), 1466 (5b), 1648 (6), 1663 (3), 2883 (10), 2911 (8), 2940 (2), 2960 (8), 2998 (3b).

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*The spectrum analysis of these compounds was carried out by Yu. P. Egorov, to whom we are greatly indebted.

b) From $Cl_3SiCH(CH_3)-CH=CH_2$, b.p. 135.5-136.8° (735 mm), and C_2H_5MgBr we prepared triethyl-(1-methylallyl)silane $(C_2H_5)_3SiCH(CH_3)-CH=CH_2$, b.p. 187° (743 mm), d_4^{20} 0.8090, n_D^{20} 1.4518, found MR 56.77, calculated MR 57.23.

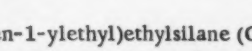
Found %: C 69.91, 69.60; H 13.16, 13.05; Si 15.90, 16.30. $C_{10}H_{22}Si$.

Calculated %: C 70.51; H 13.02; Si 16.47.

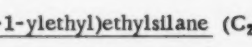
The Raman spectrum of $(C_2H_5)_3SiCH(CH_3)-CH=CH_2$ (II) contains the following frequencies*:

ν (cm^{-1}): 174 (1), 463 (2b), 515 (4b), 560 (4b), 746 (2), 797 (0), 889 (3), 968 (4), 1010 (3), 1089 (1), 1115 (3b), 1140 (1), 1164 (4), 1200 (1), 1240 (3b), 1305 (4db), 1416 (4), 1466 (3b), 1628 (5), 2880 (5), 2910 (3), 2940 (2), 2960 (3b), 3000 (2b), 3085 (0).

Among the observed frequencies of (I) frequencies of (II) are completely absent [in particular the lines characteristic for the double bond of (II) (1628 cm^{-1})]. The presence in the spectrum of (I) of other characteristic lines of the double bond (1648, 1662 cm^{-1}), which together with the frequencies 1165, 1308, 1380, 3014 cm^{-1} were observed also in the product of the ethylation of $CH_3Si(Cl)_2CH_2CH=CH-CH_3$ (Experiment 19), enables us to assume that the group $\equiv SiCH_2-CH=CH-CH_3$ in these compounds is present in both cis (1648 cm^{-1}) and trans (1662 cm^{-1}) configurations.

4) dichloro(3-cyclohexen-1-ylethyl)ethylsilane $(C_2H_5)(Cl)_2SiCH_2CH_2$  (30.6 g), b.p. 256.5° (768 mm). After vacuum fractionation the product had the following constants: b.p. 105° (3 mm), d_4^{20} 1.0612, n_D^{20} 1.4845, found MR 64.01, calculated MR 63.86.

21. See Table 3 and paper [4].

22. Dichloro(3-cyclohexen-1-ylethyl)ethylsilane $(C_2H_5)(Cl)_2SiCH_2CH_2$  The weight of crude product was 103 g. Fractionation through a column gave:

1) dichloro(3-cyclohexen-1-ylethyl)ethylsilane (85 g), b.p. 264° (746 mm), d_4^{20} 1.0675, n_D^{20} 1.4845, found MR 63.64, calculated MR 63.86.

Found %: C 50.63, 50.81; H 7.85, 7.78; Cl 29.11, 29.96; Si 11.86, 11.81. $C_{10}H_{18}SiCl_2$.

Calculated %: C 50.63; H 7.65; Cl 29.89; Si 11.83.

2) an oily residue (9 g), b.p. > 300°.

23. Chloro- and bromo-ethylmethylsilanes $(CH_3)(C_2H_5)SiHCl$, $(CH_3)(C_2H_5)SiHBr$. C_2H_5MgBr, prepared from 327 g (3 moles of C_2H_5Br and 73 g of Mg in 800 ml of dry ether, was added to 345 g (3 moles) of CH_3SiHCl_2 in 200 ml of dry ether. The mixture was heated for three hours, the precipitate was separated, and the reaction products were fractionated through a column, giving:

1) $(CH_3)(C_2H_5)SiHCl$ (93 g, i.e. 28.6%), b.p. 67.5° (748 mm); d_4^{20} 0.8830, n_D^{20} 1.4035, found MR 30.05, calculated MR 30.05.

Found %: H 8.38, 8.44; C 33.43, 33.48; Cl 31.00, 31.37; Si 26.07, 25.96. C_3H_9SiCl.

Calculated %: H 8.36; C 33.17; Cl 32.64; Si 25.83.

2) $(CH_3)(C_2H_5)_2SiH$ (22 g), b.p. 77.5° (741 mm);

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*The spectrum analysis of these compounds was carried out by Yu. P. Egorov, to whom we are greatly indebted.

3) $(CH_3)(C_2H_5)SiHBr$ (43.5 g), b.p. 90° (741 mm); d_4^{20} 1.2076, n_D^{20} 1.4373, found MR 33.23, calculated MR 33.17.

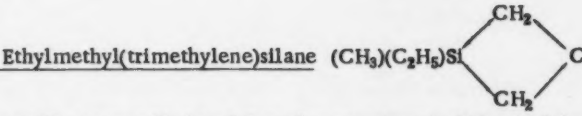
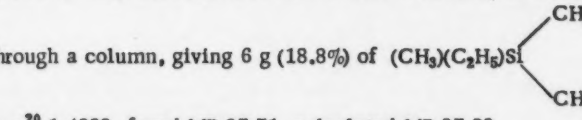
24. Chloro- and bromo-diethylsilanes $(C_2H_5)_2SiHCl$, $(C_2H_5)_2SiHBr$. C_2H_5MgBr, prepared from 327 g (3 moles) of C_2H_5Br and 73 g of Mg in 500 ml of dry ether, was added to 386 g (3 moles) of $C_2H_5SiHCl_2$ in 300 ml of dry ether. The mixture was heated for eight hours, the precipitate was separated, and the reaction products were fractionated through a column, giving:

1) $C_2H_5SiHCl_2$ (11 g), b.p. 75° (761 mm);

2) $(C_2H_5)_2SiHCl$ (121 g, i.e. 32.8%), b.p. 99° (739 mm);

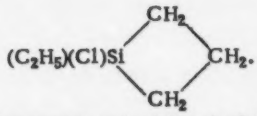
3) $(C_2H_5)_3SiH$ (11 g), b.p. 107° (750 mm);

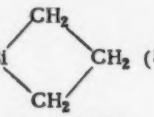
4) $(C_2H_5)_2SiHBr$ (56.5 g), b.p. 121° (750 mm), d_4^{20} 1.1903, n_D^{20} 1.4472, found MR 37.53, calculated MR 37.56.

25. Ethylmethyl(trimethylene)silane  Chloro(3-chloropropyl)ethylmethylsilane (52 g) was added to 6.8 g of magnesium in 200 ml of dry ether. The reaction mixture was heated at the boiling point of ether for five hours. The mixture was treated with water, and the ether layer was separated and dried over sodium sulfate. Ether was distilled off, and the reaction products were fractionated through a column, giving 6 g (18.8%) of  , b.p. 109° (745 mm), d_4^{20} 0.7965, n_D^{20} 1.4388, found MR 37.71, calculated MR 37.29.

Found %: H 12.30, 12.40; C 63.90, 63.92; Si 24.55, 24.52. $C_6H_{14}Si$.

Calculated %: H 12.35; C 63.08; Si 24.57.

26. Chloroethyl(trimethylene)silane  Dichloro(3-chloropropyl)ethylsilane (103 g, i.e. 0.5 mole) was added to 15 g of magnesium in 200 ml of dry ether. The reaction mixture was heated at the boiling point of ether for six hours. After separation of the precipitate and removal of ether, the reaction products were fractionated through a column and gave:

1)  (5.9 g, i.e. 8.8%), b.p. 133.5° (747 mm), d_4^{20} 0.9791, n_D^{20} 1.4570, found MR 37.45, calculated MR 36.92.

Found %: H 8.39, 8.32; C 44.73, 44.82; Cl 26.15, 25.89; Si 20.73, 20.84. $C_5H_{11}SiCl$.

Calculated %: H 8.23; C 44.60; Cl 26.33; Si 20.84 .

2) unchanged dichloro(3-chloropropyl)ethylsilane* (65 g), b.p. 207.5° (743 mm).

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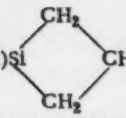
*The isolation of such a large amount of γ-chloro compound which had not reacted with magnesium after long heating in ether is evidently to be explained by the stabilizing effect of the dichlorosilylene group.

27. Chloromethyl(2-methyltrimethylene)silane  Dichloro(3-chloro--2-methylpropyl)methylsilane (102.8 g, i.e. 0.5 mole) was added to 14 g of magnesium in 200 ml of dry ether. The reaction mixture was heated at the boiling point of ether for 17 hours. After separation of the precipitate and removal of ether, the reaction products were fractionated through a column and gave:

1) chloromethyl(2-methyltrimethylene silane, (4.6 g, 6.8%), b.p. 118° (740 mm), d_4^{20} 0.9473, n_D^{20} 1.4428, found MR 37.67, calculated MR 37.22.

Found %: H 8.38, 8.31; C 45.35, 45.16; Cl 25.84, 25.58; Si 20.46, 20.57. $C_5H_{11}SiCl$.

Calculated %: H 8.23; C 44.60; Cl 26.33; Si 20.84.

2) unchanged γ-chloro compound* (31.6 g), b.p. 195-196.6° (746 mm).

SUMMARY

1. It was shown that in the addition reaction between silanes containing silicon-attached hydrogen and unsaturated compounds in presence of platinized charcoal the structures of the reactants greatly affect the course of reaction: the highest yield of addition products is given by silanes of the types $RSiHCl_2$ and R_2SiHCl and by unsaturated compounds having "active" double bonds.

2. It was found that the addition of CH_3SiHCl_2 and of $C_2H_5SiHCl_2$ to $F_2C{=}CF_2$ is accompanied by a telomerization reaction.

3. It was shown that it is possible to prepare silanes of the type RR'SiHBr by reaction of $RSiHCl_2$ with R'MgBr and to prepare also compounds having a four-membered ring including a silicon atom by the cyclization, with the aid of magnesium, of γ-chloro compounds containing at least one silicon-attached chlorine atom.

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*The previous footnote applies here also.

**In Russian.

HIGH-TEMPERATURE TRANSFORMATIONS OF n-NONANE ON A PLATINIZED ALUMINUM SILICATE IN A FLOW SYSTEM IN PRESENCE OF HYDROGEN AT HIGH PRESSURE

Kh. M. Minachev, N. I. Shuikin, L. M. Feofanova, and Yu. P. Egorov

In some of our studies [1-3] of the catalytic properties of Group VIII metals with respect to transformations of alkanes, cyclopentanes, and cyclohexanes in a flow system in presence of hydrogen at high pressure, we showed that the chemical nature of the carrier and variation in the experimental conditions substantially affect the properties of the catalyst and the character of the changes undergone by the hydrocarbons. Thus, the effect of the carrier was shown clearly in the case of the transformations of ethylcyclopentane. Over Pt-Al_2O_3 ethylcyclopentane was isomerized with ring expansion into methylcyclohexane and further dehydrogenated into toluene (the toluene content of the catalyzate was found to be 44%). Some of the hydrocarbon was isomerized into 1,2- and 1,3-dimethylcyclopentanes, and to a small extent hydrogenolysis of the five-membered ring occurred. Very different results were obtained over platinized silica gel. In this case much of the ethylcyclopentane was hydrogenolyzed with formation of normal and branched paraffins. The part played by the carrier was demonstrated also in the case of methylcyclohexane over Ru and Rh catalysts: when the carrier was SiO_2 considerable scission occurred, both of the original hydrocarbon and of its transformation products, whereas in the case of an Al_2O_3 carrier these reactions occurred to a much smaller extent.

In the further development of our investigations, it was considered to be of interest to study the specific properties of a platinum catalyst of low active-metal content on a mixed carrier (Al_2O_3 + SiO_2) under the same conditions. The carrier selected for this purpose was an industrial aluminum silicate cracking catalyst. The transformations of n-nonane were investigated in presence of this catalyst. Our experiments showed that high-temperature (400°) transformations of this hydrocarbon on a platinized aluminum silicate catalyst in a flow system in presence of hydrogen at high pressure (20 atm) proceed with a conversion of up to 100%, and they result in the formation of a considerable amount of aromatic hydrocarbons (10.2%) and of light hydrocarbons boiling up to 40° (more than 53% of the catalyzate). The content of isoparaffins in the catalyzate is 46.3%. When the reaction temperature is lowered to 360°, hydrocracking proceeds to a much smaller extent: 17.6% of hydrocarbons boiling up to 40° is obtained, and about 63% of isoparaffins; the conversion of nonane is 70.5%.

In a special experiment it was shown that the conversion of nonane at 400° and 20 atm in presence only of the aluminum silicate used as carrier is only 13%; the isoparaffin content is about 14.2%, and no aromatic hydrocarbons are formed.

EXPERIMENTAL

Carrier. The carrier used in the preparation of the catalyst was an aluminum silicate cracking catalyst from the Salavat works; its composition was 89.15% SiO_2, 10.5% Al_2O_3, 0.2% Na_2O, and 0.15% Fe_2O_3. Iron impurity was removed by treatment with boiling dilute (1 : 2) hydrochloric acid, the catalyst was washed with distilled water until a test for chloride was negative, and it was then dried at 120° and calcined in a muffle at 500° for four hours. The specific surface of the aluminum silicate*, as deter-

*The specific surface of the aluminum silicate was determined by V. A. Afanasyev, to whom the authors express their indebtedness.

TABLE 1

Properties of Nonane Catalyzate

H_2 pressure 20 atm, v 1.1 hour^{-1}, H_2: hydrocarbon = 5

Experiment No.	Catalyst	Temperature of experiment (°C)	Properties of catalyzate after removal of fraction up to 40° by distillation.		Contents of various hydrocarbons (% by weight on catalyst)						Composition of gas		Conversion of hydrocarbon (%)
			n_D^{20}	d_4^{20}	Hydrocarbons boiling up to 40°	Isopentane	n-pentane	Isoparaffins	Aromatic hydrocarbons	Unchanged nonane	H_2	C_nH_{2n+2}	
1	1% Pt on aluminum silicate	400	1.4182	0.7073	18.2	15.7	19.3	46.3	10.2	–	88.8	12.2	100.0
2	1% Pt on aluminum silicate	360	1.4075	0.7168	-	10.0	7.6	63.0	Trace	13.6	97.0	2.8	70.5
3	Aluminum silicate	400	1.4073	0.7174	-	-	-	14.2	Trace	84.0	100	-	13.0

mined by the dynamic method [4] from the adsorption isotherms of benzene at 20°, was 190 sq. m/g. Its acidity, expressed as pH, was 5.6.

Catalyst. The carrier was impregnated with a dilute solution of H_2PtCl_6 at room temperature. It was dried at 110° for five hours, and then placed in a glass tube and reduced in a stream of electrolytic hydrogen at 330° for ten hours. The acidity of the reduced catalyst, expressed as pH, was 6.15.

Nonane. The nonane was prepared by the dehydration of nonyl alcohol and subsequent hydrogenation of the resulting nonene over Raney nickel in an autoclave. After being purified and distilled through a column of 35 theoretical plates, the hydrocarbon had the following properties: b.p. 149.5-150.6° (760 mm), n_D^{20} 1.4059, d_4^{20} 0.7178; aniline point 74.8; found MR 43.76; for C_9H_{20} calculated MR 43.87. For this hydrocarbon the literature [5] gives b.p. 150.77° (760 mm), n_D^{20} 1.4054, d_4^{20} 0.7176; aniline point 74.9.

Apparatus and Experimental Conditions. The apparatus used was described in a previous communication [6]. The experiments were carried out at 400° and 360° in presence of hydrogen at 20 atm at a space velocity of feed of nonane of 1.2 liters per liter of catalyst per hour and with a ratio of hydrocarbon to hydrogen of 1 : 5. In each experiment, 120-150 g of hydrocarbon was taken.

Investigation of Catalyzates. The products of the catalytic treatment of nonane were investigated with the aid of methods of chromatographic adsorption, precise rectification, Raman spectra, and infrared spectra. The gaseous products were analyzed in an Orsat-Lunge apparatus and in a chromathermograph.

The properties of the catalyzates and the contents of hydrocarbons of various classes (calculated on the amount of catalyzate) are presented in Table 1. It will be seen that lowering of the temperature of the experiment by 40° (from 400° to 360°) results in the disappearance of the fraction boiling up to 25° and a reduction by 6% in the isopentane content and by 11.7% in the pentane content; at the same time the content of saturated hydrocarbons in the gas is reduced to one-third. For the given catalyst, therefore, the optimum treatment temperature is 360°, at which there is a high conversion of hydrocarbon, a considerable yield of isoparaffins (63%), and only a small amount of gas formed.

Catalyzates, both from 400° experiments and from 360° experiments, were subjected to debutanization. The gases obtained were analyzed chromathermographically. The gas obtained in the first experi-

TABLE 2

Fractional Composition and Properties of Aromatic Hydrocarbons Isolated from Nonane Catalyzate Obtained on Platinized Aluminum Silicate at 400°

Fraction No.	Properties of Fraction			Weight of fraction (g)	Yield (% by weight)		Results of spectrum investigation
	Boiling limits (°C)	n_D^{20}	d_4^{20}		on catalyst	on original hydrocarbon	
I	92-109	1.4835	-	0.6	0.6	0.42	Not investigated
II	109-112	1.4963	0.8664	1.6	1.5	1.12	Toluene
III	112-135.0	1.4963	-	0.7	0.7	0.5	
IV	135-147.0	1.4950	0.8605	1.6	1.5	1.12	5% o-, 30% p-, and 65% m-xylene
V	147-151	1.4960	-	0.42	0.41	0.29	Not investigated
VI	151-165.3	1.4985	0.8683	4.1	4.0	2.9	The main product was 1,2,4-trimethylbenzene; other products, formed in smaller amounts, were o- and m-ethyltoluenes and, probably, mesitylene

Note. The fraction was carried out with addition of 5 ml of decahydronaphthalene (b.p. 185-188°).

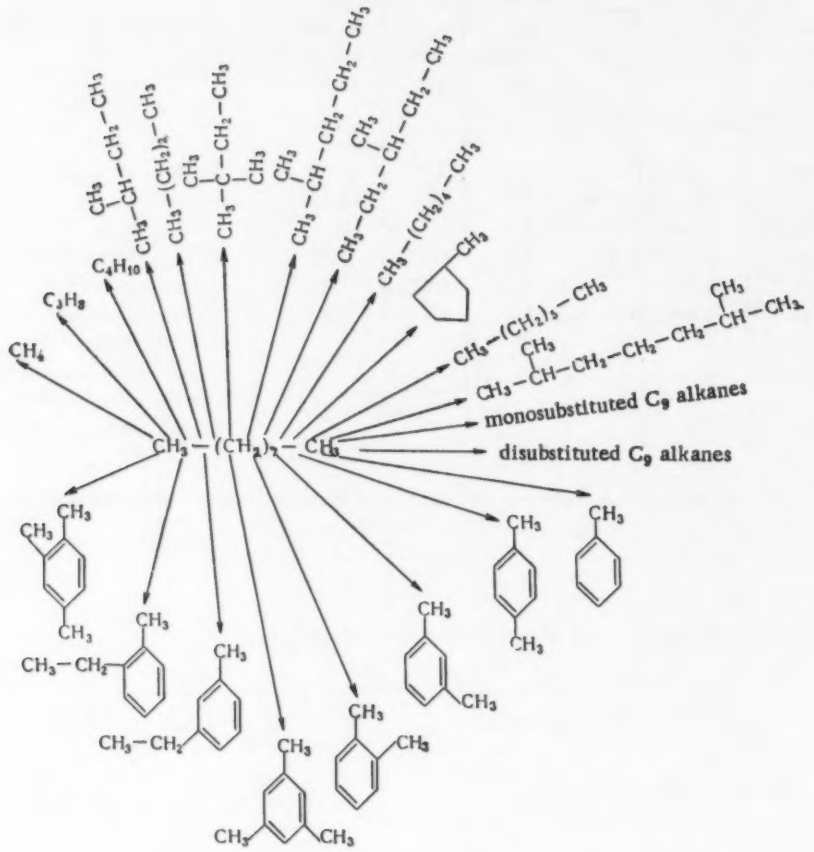
TABLE 3

Results of the Spectrum Investigation of the Nonane Catalyzate

Boiling limits of fraction (°C)	Hydrocarbon identified	Catalyst		
		Pt on aluminum silicate		Aluminum silicate
		Temperature of experiment (°C)		
		400	360	400
		Amount % by weight on catalyst		
50 - 60	2,2-Dimethylbutane	0.2	0.1	-
60 - 65	2-Methylpentane 3-Methylpentane	6.9	3.7	-
65 - 70	Hexane	2.1	1.2	-
90 - 100	Heptane	1.6	1.2	-
125 - 135	Mainly 2,6-dimethylheptane	1.8	4.5	2.2
135 - 140	Mixture of mono- and di-substituted C_9 hydrocarbons in equal amounts	2.2	8.4	2.1
140 - 145	Mainly monosubstituted C_9 hydrocarbons	1.8	25.6	4.5
145 - 149	Mixture of n-nonane and monosubstituted C_9 alkanes	-	5.3	10.9
149 - 151 (766)	Nonane	-	11.0	64.5

Note. Judging from the aniline point (60.5°), the 65-70° fraction contained 32-33% of methylcyclopentane.

ment (400°) consisted of 62% of propane and 37% of butane, and those obtained in the second (360°) of 30% of butane and 70% of propane. The hydrocarbons boiling in the range 25-33° (n_D^{20} 1.3540, d_4^{20} 0.6173) and in the range 33-40° (n_D^{20} 1.3580, d_4^{20} 0.6272) corresponded in properties to isopentane and pentane. The identities of the hydrocarbons isolated from the catalyzate obtained in the first experiment and boiling up to 25° were not investigated further; the product probably consisted of a mixture of butanes and neopentane.



The aromatic hydrocarbons (10 g) isolated from the nonane catalyzate (Experiment 1) by adsorption on silica gel were fractionated through a column of 35 theoretical plates. Their fractional composition and properties are given in Table 2. The same table gives results of the spectrum analysis of some of the fractions.

The paraffins remaining after the separation of aromatic hydrocarbons were fractionated, and the fractions were then investigated with the aid of Raman and infrared spectra. Table 3 gives the results of this spectrum investigation with an indication of the amounts of the hydrocarbons found, expressed as per cent by weight of the catalyzate. We did not succeed in identifying some of the fractions owing to the small amounts in which they were formed.

On the basis of this investigation of the catalyzates we propose the accompanying scheme for the transformations of nonane under the given conditions in presence of platinized aluminum silicate.

SUMMARY

1. A study was made of the catalytic properties of a platinized aluminum silicate catalyst containing 1% of finely dispersed platinum in the transformations of n-nonane in a flow system at 400° and 360° in presence of hydrogen at a pressure of 20 atm. It was shown that, under the given conditions, the hydrocarbon undergoes various far-reaching transformations and the character and extent of these transformations are considerably dependent on the temperature of the experiment.

2. It was found that in contact with the above catalyst at 400° the conversion of nonane is 100%. The main reactions are isomerization, hydrocracking, and dehydrocyclization of the original hydrocarbon. The extent to which hydrocracking occurs is considerably reduced when the temperature is lowered to 360°; at this temperature the yield of isoparaffins is about 63%.

3. At 400° in presence of hydrogen at 20 atm, the conversion of nonane in presence of an aluminum silicate catalyst is only 14%.

4. The platinized aluminum silicate catalyst investigated may be used in the reforming of gasolines with the object of raising their octane ratings.

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* In Russian.

OXIDE-METAL CATALYSTS FOR THE REFORMING OF GASOLINES

COMMUNICATION 1. REFORMING OF THE 96-114° FRACTION OF ILSK-KHADYZHENSK PETROLEUM OVER A PLATINUM-SILICA CATALYST

Kh. M. Minachev, N. I. Shuikin, M. A. Ryashentseva, and N. F. Kononov

The catalytic reforming of gasolines and ligroins of petroleums of various origins, which is one of the most important branches of petroleum processing, has the object of preparing high-octane aviation and motor fuels and concentrates of aromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylenes). The conversion of the C_6–C_8 naphthenes and paraffins present in the gasolines into aromatic hydrocarbons and isoparaffins (with the same or lower number of carbon atoms) proceeds in presence of metal (Pt, Pd, and others) and oxide (Cr_2O_3, MoO_3, and others) catalysts supported by carriers such as Al_2O_3, SiO_2, and Al_2O_3–SiO_2. These metals, oxides, and carriers, which, individually have either hydrogenating and dehydrogenating properties (Pt, Pd), mainly dehydrogenating properties (MoO_3), or cracking properties (aluminum silicate), when considered as a whole are seen to possess not only these individual functions, but also in most cases isomerizing properties. Such catalysts are known as bifunctional catalysts [1,2].

The main reactions occurring in presence of these catalysts are dehydrogenation of cyclohexanes, isomerization of n-paraffins and their dehydrocyclization into aromatic hydrocarbons, isomerization of cyclopentanes into cyclohexanes and further dehydrogenation of the latter, and finally, hydrocracking of n-paraffins with formation of n- and iso-paraffins of lower molecular weight. The main reactions are accompanied by side reactions (desulfurization and demethylation). A leading part in the discovery of most of these reactions has been played by Soviet scientists [3-6].

In recent years, work has been published, both here and abroad, on the catalytic transformations of individual C_6–C_8 hydrocarbons of petroleum origin [7-14] and their natural mixtures (gasolines and ligroins [15-17] at 450-480° in presence of hydrogen at high pressure (up to 60 atm) so as to suppress the formation of deposits of coke and sulfur on the catalyst since these result in loss of catalyst activity.

The transformation (reforming) of gasolines is greatly affected not only by the composition of the catalyst, but also by the conditions under which the process is carried out. The choice of conditions (temperature, pressure, time of contact, ratio of recirculating gases to intake of material) depends on the composition of the starting material and on the purpose of the process (preparation of high-octane motor or aviation fuel or of concentrates of aromatic hydrocarbons).

Two of the present authors with co-workers [11-13] showed that platinized silica gel has good catalytic properties for the transformations of some individual hydrocarbons. Thus, heptane at 460° in presence of hydrogen at 20 atm in a flow system underwent dehydrocyclization with formation of aromatic hydrocarbons (23% yield), isomerization, and hydrocracking. Under the same conditions methylcyclohexane gave toluene (95% yield) and ethylcyclopentane underwent hydrogenolysis and partial isomerization with ring expansion and subsequent dehydrogenation.

The present investigation had the object of studying the possibilities of using platinized silica gel for the reforming of 96-114° fractions obtained from a straight Ilsk-Khadyzhensk gasoline and also the object of establishing the optimum procedure for a maximum yield of aromatic hydrocarbons. At the same time the stability of the catalyst was studied under the selected conditions of processing.

Preparation of Catalyst. A catalyst of 0.5% platinum content was prepared by impregnation of silica gel with chloroplatinic acid solution. The silica gel (from the Voskresensk Chemical Combine) was previously ground to a grain size of 1.5-2.5 mm, treated at boiling with hydrochloric acid, washed free from chloride with distilled water, dried, and calcined at 500° for two hours in a muffle; 300 ml of the catalyst prepared in this way was placed in the catalysis vessel.

Characteristics of the Original Gasoline Fraction. As raw material we used a fraction of b.p. 96-114° from straight-run gasoline derived from Ilsk-Khadyzhensk petroleum; this had n_D^{20} 1.4115 and d_4^{20} 0.7392, and it contained 6% of aromatic hydrocarbons by volume and 0.0025% of sulfur.

Engler Fractionation

Start of boiling	96.0°	60%	100.0°
5% -	97.0°	70% -	101.0°
10% -	97.0°	80% -	103.0°
20% -	98.0°	90% -	105.0°
30% -	99.0°	97.5% -	114.0°
50% -	100.0°	End of boiling	114.0°

Group composition of the fraction: naphthenes 39.0% by volume, paraffins 55.0% by volume, and aromatics 6.0% by volume.

Apparatus. The reforming was carried out in a block reactor; this had electrical heating with automatic control of temperature within ± 2°. The measurement and control of temperature were effected with the aid of thermocouples and electronic potentiometers. The EYaIT stainless steel catalysis tube (internal diameter 40 mm, height 800 mm) was fixed in an aluminum block which would maintain temperatures of up to 500°.

Below we give a diagram of the flow apparatus for work under pressures of up to 50 atm with recirculation of gaseous products. The raw material is fed from a measuring device 3 with the aid of a pump 4 into

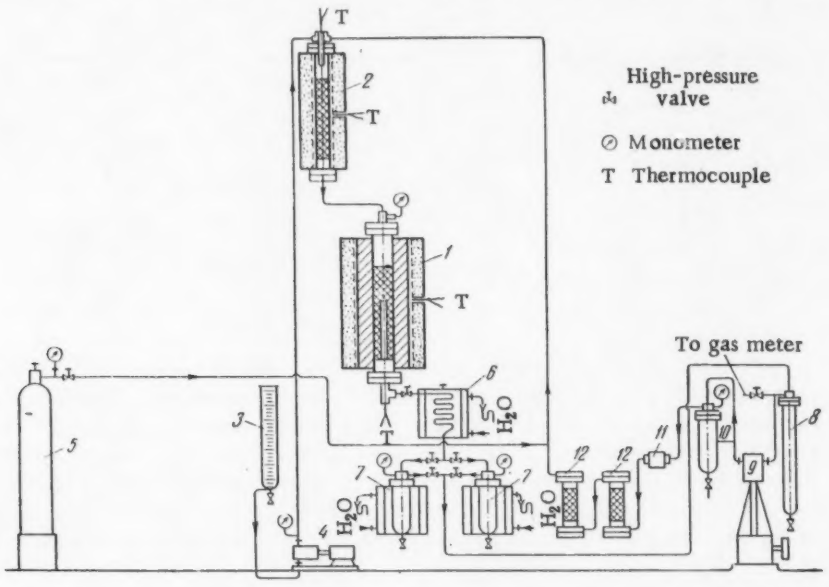

Diagram of apparatus for reforming of gasolines: 1) reactor; 2) evaporator; 3) measuring device; 4) pump for liquid; 5) cylinder of hydrogen; 6) condenser; 7) separators; 8) trap-absorber; 9) circulating pump for gas; 10) oil separator; 11) gas meter; 12) trap-adsorbers.

the evaporator 2. Before the beginning of the process hydrogen passes into the evaporator 2, in which it is mixed with gasoline vapor. The vapor-gas mixture passes to the reactor 1. The reaction products pass to the condenser 6 and further to one of the gas-separator receivers 7, in which the liquid catalyzate is separated from the gaseous reaction products. The latter then pass to the trap-absorber 8, which contains diethanolamine for the absorption of hydrogen sulfide present in the gas mixture. The gaseous products are taken from the trap with the aid of the circulating pump 9, through the oil separator 10, through the gas meter 11 and the adsorber-traps 12 (for separation from oil vapor; filled with activated charcoal), through the evaporator 2, and so into the reactor 1. The excess of gaseous products pass into the atmosphere through an activated charcoal trap and a gas meter. For the purposes of dosage, circulation, and the checking of the consumption of liquid and gaseous materials use was made of a) a piston pump 4 for liquid passing 0.1-1 liter/hour at 50 atm; b) a gas-circulating pump 9 with a controllable throughput of 600-3500 liters/hour at pressures of up to 50 atm; c) a gas meter 11, the design of which was based on that of the wet gas meter (kerosene was used as sealing liquid). The gas meter mechanism was enclosed in a steel case designed for working pressures of up to 50 atm. The consumption of circulating gas was determined from the number of rotations of the meter in unit time.

Experimental Procedure. The temperature in the reactor was raised to the required value (450-480°) while a feeble current of hydrogen was maintained; the pressure of hydrogen was then raised to the required value. The piston pump, which had been previously adjusted so as to feed raw material at the required rate*, and the circulatory gas pump were switched on; this established the required molar ratio of hydrogen and raw material (H_2 : HC). The mixture was passed over the catalyst for one hour (pre-experiment period), and in the course of this time constancy of rate of feed, temperature, and pressure was established. After removal of the liquid catalysis products that had accumulated in the pre-experiment period, an 8-10-hour experiment was generally carried out.

TABLE 1

Effect of Pressure on the Degree of Conversion of the 96-114° Fraction

(450°, V = 0.9-1.0 hour^{-1}, H_2: HC = 5)

Experiment No.	Pressure (atm)	n_D^{20}	d_4^{20}	Content of aromatic hydrocarbons (% by volume)
15	10.0	1.4305	0.764	33.5
8	15.0	1.4290	0.762	31.0
12	20.0	1.4285	0.760	29.5
18	30.0	1.4260	0.756	27.0
16	35.0	1.4260	0.756	27.0

TABLE 2

Effect of the Ratio H_2 : HC on the Degree of Conversion of the 96-114° Fraction

(450°, 20 atm, V = 0.9-1.0 hour^{-1})

Experiment No.	Ratio H_2 : HC	n_D^{20}	d_4^{20}	Content of aromatic hydrocarbons (% by volume)
12	5.7	1.4285	0.760	29.5
17	7.2	1.4290	0.762	30.0
13	10.8	1.4270	0.758	28.5

Analysis of Starting Materials and Products. In the catalyzates, and also in the starting material, determinations were made of refractive index, density, content of aromatic hydrocarbons (sulfuric acid method), and content of sulfur compounds (lamp method); the same materials were also subjected to Engler fractionation. The gaseous products were analyzed in an Orsat-Lunge apparatus and were found to contain 98% of hydrogen. The losses of gasoline with the procedure adopted were found to be 2-3% on the weight of raw material. Studies were made of the effect of total pressure, temperature, rate of feed of gasoline (96-114° fraction), and relative amounts of hydrogen and gasoline on the content of aromatic hydrocarbons in the catalyzate.

*Space velocity of feed was measured in liters of starting material per liter of catalyst per hour (V in hour^{-1}).

Pressure. The effect of total pressure on the content of aromatic hydrocarbons in the catalyzate was investigated at V = 0.9-1.0 hour^{-1}, 450°, and H_2 : HC = 5. The results are given in Table 1.

The increase in the amount of aromatic hydrocarbons results mainly from the dehydrogenation of cyclohexanes (special experiments showed that the original fraction contained about 24% of six-membered naphthenes) and only to an insignificant extent (3.5%) from reactions of hydrocarbons of other classes. The reduction in the content of aromatic hydrocarbons with rise in pressure is in close accord with the effect of pressure on the equilibrium composition of the system methylcyclohexane--toluene in the range 300-500° [18]. Thus, whereas methylcyclohexane is converted completely into toluene at 450° in presence of hydrogen at 20 atm, the conversion of methylcyclohexane is only 90% at 35 atm.

It is known [16,19] that rise in pressure favors the preservation of catalyst activity while somewhat reducing the extent to which dehydrogenation occurs. In further experiments we used a pressure of 20 atm, at which the degree of dehydrogenation was only slightly reduced. It is known also that rise in pressure results in increased hydrocracking of paraffins. However, with rise in pressure from 10 to 35 atm, no appreciable increase in gas formation occurred (it remained at the former very low level), from which we may conclude that the contribution of hydrocracking reactions in presence of a 0.5% Pt-SiO_2 catalyst is very small.

Ratio H_2 : HC. The effect of the ratio H_2 : HC on the content of aromatic hydrocarbons in the catalyzate was investigated at 450°, 20 atm, and V = 0.9-1.0 hour^{-1}. The ratio was varied from 5 to 10, lower values not being attained for technical reasons. The results are given in Table 2.

Table 2 shows that increase in the ratio H_2 : HC has an insignificant effect on the content of aromatic hydrocarbons in the catalyzate. In further experiments we adopted the ratio of 7.2.

Space Velocity. The effect of the space velocity of the supply of the original gasoline fraction on the content of aromatic hydrocarbons in the catalyzate was investigated at 450°, 20 atm, and H_2 : HC = 7.2. The space velocity V was varied from 0.8 to 2.15 hour^{-1}. The results are given in Table 3.

TABLE 3

Effect of Space Velocity on Degree of Conversion of the 96-114° Fraction (450°, 20 atm, H_2 : HC = 7.2)

Experiment No.	Space velocity (hour^{-1})	n_D^{20}	d_4^{20}	Content of aromatic hydrocarbons (% by volume)	Boiling range of catalyzate (°C)
7	0.8	1.4290	0.762	30.0	83—127
15	1.05	1.4270	0.758	28.5	86—117
24	1.55	1.4240	0.753	22.0	91—115
25	2.15	1.4235	0.752	21.0	91—114

It follows from Table 3 that the content of aromatic hydrocarbons is lowered by 9% when the rate of feed is increased 2.7 times. As the optimum rate of feed of the starting material is closely associated with the productivity of unit working volume of the catalysis reactor for a given conversion of the fraction (which may not be high), in striving to obtain the maximum yield of aromatic hydrocarbons, we adopted a space velocity in the range 0.8-1.0 hour^{-1}. However, reduction of V to 0.8 hour^{-1} favors some lowering of the fractional composition of the catalyzate (start of boiling 83° instead of 96° for the starting material, see Table 3), which indicates appreciable increase in the extent of hydrocracking.

Temperature. It is known [20] that temperature has a considerable effect on the degree of conversion of both naphthenes and paraffins, so that the choice of optimum temperature was particularly important. Since in the transformations of the 96-114° fraction over Pt—SiO_2 at 450° no appreciable hydrocracking of paraffins was observed (and therefore no appreciable gas formation), a rise of temperature of 20-30° should not bring about hydrocracking reactions, but only increase the rate of dehydrogenation.

TABLE 4

Effect of Temperature on the Transformations of the 96-114° Fraction

(20 atm, V = 1.0 hour^{-1}, H_2 : HC = 7.2)

Experiment No.	Temperature (°C)	n_D^{20}	d_4^{20}	Content of aromatic hydrocarbons (% by volume)
27	450	1.4255	0.754	25.5
29	470	1.4260	0.756	27.0
32	480	1.4285	0.760	29.5

The effect of change in temperature in the range 450-480° on the content of aromatic hydrocarbons in the catalyzate was investigated at 20 atm, V = 1 hour^{-1}, and H_2 : HC = 7.2. As the catalyzate had already been in use in the reaction for 152 hours, its activity was somewhat reduced, which explains the reduced content of aromatic hydrocarbons in the catalyzate (reduced from 30% to 25.5%) at 450°. The results are given in Table 4.

Table 4 shows that rise in temperature from 450° to 480° raised the content of aromatic hydrocarbons to 29.5%. The extent of gas formation remained at the same level (2%). Rise in temperature, therefore, results in increase in the dehydrogenating activity of the catalyst and has no appreciable effect on gas formation during the processing of petroleum fractions in presence of the catalyst 0.5% Pt—SiO_2. The catalyst was in reaction at 480° for about 150 hours without appreciable loss in activity.

SUMMARY

1. In the aromatization of the straight-run 96-114° gasoline fraction of Ilsk-Khadyzhensk petroleum, optimum processing conditions were established (480°, 20 atm, V = 1 hour^{-1}, H_2 : HC = 7.2) for maximum yield of aromatic hydrocarbons resulting from dehydrogenation of cyclohexanes.

2. It was shown that, under the processing conditions adopted, the catalyst 0.5% Pt—SiO_2 is mainly a dehydrogenating catalyst. Its isomerizing, dehydrocyclizing, and hydrocracking properties are extremely feeble, this being indicated by the insignificant increase in the amount of aromatic hydrocarbons at the expense of hydrocarbons of other classes other than cyclohexanes and by the small extent of gas formation (not more than 2%).

3. The catalyst can be applied in the preparation in high yield of concentrates of aromatic hydrocarbons from low-sulfur gasolines having a naphthene or mixed basis.

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STERIC FACTOR IN ELECTROPHILIC SUBSTITUTIONS OF AROMATIC HYDROCARBONS

COMMUNICATION 2

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We have previously reported [1,2] an investigation of orientation in the chloromethylation of aromatic compounds. It was shown that in the chloromethylation of a series of aromatic hydrocarbons (toluene, ethylbenzene, cumene, and tert-butylbenzene) there is a gradual reduction in the amount of o-isomer formed and a corresponding increase in the amount of p-isomer. This was attributed to the increase in the bulk of the alkyl substituent (steric factor).

In order to elucidate the effect of the structure of the substituent in the benzene nucleus on the orientation of electrophilic substitution in greater detail, it was considered to be of interest to extend the range of substituent radicals, in particular to various radicals having a normal chain or a chain in which branching occurs at a greater distance from the benzene nucleus than in the case of cumene; also to radicals of cyclic structure. With this object, in addition to the chloromethylation of the above-named aromatic hydrocarbons, we chloromethylated also propylbenzene, butylbenzene, isobutylbenzene, and cyclohexylbenzene under strictly comparable conditions. There are references in the literature to the exclusive formation of p-(chloromethyl) derivatives of the hydrocarbons enumerated above [3]. However, our more detailed investigation of the structures of the products of the chloromethylation of these hydrocarbons showed that in all cases mixtures of o- and p-(chloromethyl) derivatives are formed. The compositions of these mixtures of isomers were established, in the way described previously [1,2], by oxidation with chromium trioxide in acetic acid and comparison of the yields of terephthalic acid with the yield of this acid obtained in the oxidation of the pure p-isomer or the product of the chloromethylation of toluene, the isomer composition of which was firmly established previously [1]. This method of proving the composition of mixtures of o-, m-, and p-disubstituted benzenes is based on the well-known fact that chromium trioxide oxidizes only the m- and p-isomers into the corresponding benzenedicarboxylic acids, whereas the o-isomer is completely oxidized with breakdown of the benzene ring. Direct proof of the presence of o-(chloromethyl) derivatives in these cases was obtained by oxidation of the mixtures with dilute nitric acid at 200° [4] and isolation of pure phthalic and terephthalic acids. In this way it was found that the mixture of chloromethylation products obtained from propylbenzene consisted of 78.5% of p-isomer and 21.5% of o-isomer. The mixture obtained in the chloromethylation of butylbenzene was of the same composition. In the chloromethylation of isobutyl- and cyclohexyl-benzenes, mixtures of identical composition were again obtained, and this composition was almost the same as that obtained in the chloromethylation of cumene, i.e. 84% of p-isomer and 16% of o-isomer.

From a comparison of results on the composition of mixtures obtained in the chloromethylation of propyl- and butyl-benzenes with the analogous data obtained previously [1,2] for toluene and ethylbenzene (Table 1) it follows that increase in the length of an n-alkyl chain results in increased steric hindrance at the o-position as we pass from toluene to propylbenzene, but with further increase in length (butylbenzene) there is no further diminution in the amount of o-isomer formed. In other words, in chloromethylation reactions the screening effect of an n-alkyl substituent on the o-position of the aromatic nucleus does not increase appreciably beyond propyl.

Our investigation, therefore, provides a general picture of orientation in the chloromethylation of alkylbenzenes as a function of the character of the alkyl radical (Table 1).

TABLE 1

Hydrocarbon chloromethylated	Proportions of chloromethyl derivatives (%)	
	o-Isomer	p-Isomer
$C_6H_5CH_3$	51.7	48.3
$C_6H_5C_2H_5$	30	70
$C_6H_5C_3H_7$-*n*	21.5	78.5
$C_6H_5C_4H_9$-*n*	21.5	78.5
$C_6H_5C_4H_9$-*i*	16	84
$C_6H_5C_6H_{11}$	16	84
$C_6H_5C_3H_7$-*i*	15	85
$C_6H_5C_4H_9$-*tert*	0	100

TABLE 2

Hydrocarbon nitrated	Composition of mononitro derivatives (%)	
	o-Isomer	p-Isomer
$C_6H_5CH_3$	67.5	32.5
$C_6H_5C_2H_5$	55.6	44.4
$C_6H_5C_3H_7$-*n*	56	44
$C_6H_5C_4H_9$-*n*	57	43
$C_6H_5C_4H_9$-*i*	57	43
$C_6H_5C_3H_7$-*i*	39.5	60.5
$C_6H_5C_4H_9$-*tert*	11.8	79.5 *

* Together with 8.7% of m-isomer [7].

In order to preserve complete identity of conditions in the chloromethylation of all these hydrocarbons, the procedure adopted was generally that used for the chloromethylation of toluene [1]. Hydrocarbons having heavier substituents then gave chloromethylation products in a lower yield than in the case of toluene. It was shown that, in the case of cumene and cyclohexylbenzene, the yield can be increased by addition of acetic and orthophosphoric acids to the reaction mixture [5]; it was found that the relative amounts of isomers obtained in this way were the same as in the absence of the additives.

It was of interest to examine other electrophilic substitutions in their relation to the regularities observed in the ortho-para ratio in the chloromethylation of alkylbenzenes. With this object we studied the nitration of propyl-, butyl-, and isobutyl-benzenes in supplementation of earlier work on the nitration of toluene, ethylbenzene, and cumene [6]. The compositions of the mixtures formed were determined by the previously used method of oxidation with chromium trioxide in acetic acid [6]. In this way it was shown that in the nitration of propylbenzene the mononitro derivatives formed consisted of 56% of o-isomer and 44% of p-isomer; in the nitration of butyl- and isobutyl-benzenes the mononitro derivatives obtained consisted of 57% of o-isomer and 43% of p-isomer. m-Isomers, which might have been present in very small amounts, were not determined.

The results make it possible to supplement the existing picture [6] of the dependence of orientation in nitration on the character of the alkyl substituent in the benzene nucleus (Table 2).

Table 2 shows that the steric effect of an n-alkyl radical on orientation in nitration remains unchanged after ethylbenzene, and not after propylbenzene as in the case of chloromethylation.

Comparison of Tables 1 and 2 shows that in the chloromethylation and nitration of alkylbenzenes there is the same tendency for progressive reduction in the amount of o-isomer and corresponding increase in the amount of p-isomer as the steric effect of the alkyl substituent increases. However, in chloromethylation this steric effect is more clearly expressed, and the amount of o-isomer obtained in the chloromethylation of any alkylbenzene is always considerably less (and the amount of p-isomer is correspondingly greater) than in the case of nitration of the same hydrocarbon.

This interesting regularity is evidently to be explained by differences in the spatial structures and sizes of the attacking agents in these reactions [6,8]. Thus, the smaller nitronium cation ($^+NO_2$) in nitration reactions is less "sensitive" to the steric effect of the alkyl substituent than the hydroxymethyl cation ($^+CH_2OH$) in chloromethylation reactions [9]. The nitronium cation, therefore, has a much greater penetrating power at a hindered o-position than the hydroxymethyl cation, a fact that explains the great difference in ortho-para ratio in nitration and chloromethylation. A still clearer picture of orientation is observed in the Friedel-Crafts reaction, which results in the exclusive formation of p-isomers even in the case of toluene [10]. The complete absence of o-isomers in this reaction is to be explained by the inability of the reacting complex ($AlCl_3 \cdot RCOCl$) to penetrate to an o-position, even to the o-position to a methyl group.

EXPERIMENTAL

Propyl-, butyl-, and isobutyl-benzenes used in this work were obtained by modified Kizhner reduction of propio-, butyro-, and isobutyro-phenone, respectively. Cyclohexylbenzene was obtained by reaction of cyclohexanone with phenylmagnesium bromide and subsequent dehydration and hydrogenation.

Chloromethylation of Propyl-, Butyl-, and Isobutyl-benzenes and Cyclohexylbenzene.

a) Hydrogen chloride was passed for 25 hours into a rapidly stirred mixture of 80 ml of concentrated hydrochloric acid, 20 g of paraform, and 60 g of propylbenzene at about 55°. The reaction mixture was extracted with ether, and the ether extract was washed with water, with sodium bicarbonate solution, and again with water and then dried over calcium chloride. Solvent and unchanged propylbenzene (29.1 g) were distilled off, and vacuum distillation of the residue gave 27.6 g of a mixture of propylbenzyl chlorides, b.p. 94-97° (10 mm), yield 74% on the amount of propylbenzene that reacted. The residue from the distillation amounted to 1.1 g.

b) Under analogous conditions 67 g of butylbenzene gave 15 g (76% on the amount of butylbenzene that reacted) of a mixture of butylbenzyl chlorides, b.p. 105-109° (7 mm); 52.5 g of unchanged butylbenzene was recovered. The residue from the distillation amounted to 0.9 g.

c) Under the same conditions 67 g of isobutylbenzene gave 13.2 g (65% on the amount of isobutylbenzene that reacted) of a mixture of isobutylbenzyl chlorides, b.p. 107-110° (10 mm); 52 g of unchanged isobutylbenzene was recovered. The residue from the distillation amounted to 1 g.

d) Under the same conditions 60 g of cyclohexylbenzene, 30 g of paraform, and 100 ml of concentrated hydrochloric acid gave 11.1 g (72% on the amount of cyclohexylbenzene that reacted) of a mixture of cyclohexylbenzyl chlorides, b.p. 147-151° (8 mm); 48.1 g of unchanged cyclohexylbenzene was recovered. The residue from the distillation amounted to 0.9 g.

Chloromethylation of Cyclohexylbenzene and Cumene in presence of Orthophosphoric and Acetic Acids.

a) Hydrogen chloride was passed for 25 hours through a vigorously stirred mixture of 40 g of cyclohexylbenzene, 10 g of paraform, 16.5 g of crystalline orthophosphoric acid, 33 ml of acetic acid, and 46 ml of concentrated hydrochloric acid at 75-80°. The usual treatment gave 17.7 g (93% on the amount of cyclohexylbenzene that reacted) of a mixture of cyclohexylbenzyl chlorides, b.p. 130-133° (3 mm); 20.5 g of unchanged cyclohexylbenzene was recovered. The residue from the distillation amounted to 1.1 g.

b) Under analogous conditions 30 g of cumene, 15 g of paraform, and the same amounts of the other components gave 25.8 g (61% on the amount of cumene taken for reaction) of a mixture of isopropylbenzyl chlorides, b.p. 92-94° (8 mm). The residue from the distillation amounted to 2.7 g.

Oxidation of Chloromethylation Products with Chromium Trioxide.

a) A mixture of 2.5 g of the chloromethylation products from propylbenzene, 15 g of chromium trioxide, 45 ml of water, 45 ml of acetic acid, and 15 ml of concentrated sulfuric acid was heated under reflux until exothermic oxidation set in. When heat ceased to be evolved, the reaction mixture was boiled further for one hour. Cooling, filtration, and drying gave 1.65 g (67%) of terephthalic acid. In a repeat experiment 1.63 g of terephthalic acid was obtained. From a comparison of this result with that of the oxidation of the chloromethyl derivatives of toluene [1] under strictly analogous conditions, it follows that the chloromethylation of propylbenzene gives a mixture of propylbenzyl chlorides containing 78.5% of p-isomer and 21.5% of o-isomer.

b) Oxidation under analogous conditions of 2.5 g of the mixture of chloromethyl derivatives of butylbenzene gave 1.52 g (67%) of terephthalic acid. In a repeat experiment 1.51 g of terephthalic acid was obtained. The yield of terephthalic acid indicates that the composition of the mixture oxidized corresponds to that of the mixture obtained from propylbenzene.

c) Oxidation under the same conditions of 2.5 g of the mixture of chloromethyl derivatives of isobutylbenzene gave 1.63 g (71.8%) of terephthalic acid, which corresponds to contents of 84% of p-isomer and 16% of o-isomer in the mixture. In a repeat experiment 1.63 g of terephthalic acid was obtained.

d) From 2.5 g of the mixture of chloromethyl derivatives of cyclohexylbenzene, 1.42 g of terephthalic acid was obtained. A repeat experiment gave 1.44 g of terephthalic acid. The average yield was 71.8%, which corresponds to 84% of p-isomer and 16% of o-isomer in the mixture. In the oxidation of 2.5 g of the mixture of chloromethyl derivatives of cyclohexylbenzene prepared in presence of orthophosphoric and acetic acids, 1.43 g of terephthalic acid was isolated.

e) Under the same conditions 2.45 g of the mixture of chloromethyl derivatives of cumene gave 1.75 g (72.4%) of terephthalic acid [2].

In all cases the terephthalic acid obtained was identified through its dimethyl ester, m.p. 141-142°.

Oxidation of Chloromethylation Products with Dilute Nitric Acid at 200°.

a) A mixture of 70 ml of 20% nitric acid and 4 g of the chloromethylation products from propylbenzene was prepared in a 200-ml rotating autoclave and was then agitated at 200° for 90 minutes. When oxidation was complete, 2.6 g of terephthalic acid was filtered from the cooled reaction mixture and 0.4 g of phthalic acid was separated from the mother liquor after evaporation to small bulk; the latter was identified through its anilide, m.p. 208-210°, undepressed by admixture of a known sample. The total yield of acids was 77%.

b) Oxidation under analogous conditions of 4 g of the mixture of chloromethyl derivatives of butylbenzene with 75 ml of 20% nitric acid gave 2.1 g of terephthalic acid and 0.6 g of phthalic acid, which was again identified through its anilide. The total yield of acids was 75%.

c) Oxidation under analogous conditions of 4 g of the mixture of chloromethyl derivatives of isobutylbenzene with 75 ml of 20% nitric acid gave 2.53 g of terephthalic acid and 0.68 g of phthalic acid, which was identified through its anilide. The total yield of acids was 88%.

d) Oxidation under analogous conditions of 4 g of the mixture of chloromethyl derivatives of cyclohexylbenzene with 85 ml of 20% nitric acid gave 2.51 g of terephthalic acid and 0.4 g of phthalic acid, which was identified through its anilide. The total yield of acids was 91%.

In all these cases phthalanilide had m.p. 208-209°, undepressed by admixture of a known sample.

Nitration of Propyl-, Butyl-, and Isobutyl-benzenes.

a) Nitration mixture (32 ml of concentrated sulfuric acid and 25 ml of nitric acid, sp. gr. 1.42) was added over a period of one hour to stirred propylbenzene (30 g). The reaction temperature was maintained at 25-30°. When addition of nitration mixture was complete, the reaction mixture was poured into water, the precipitated oil was separated, the aqueous layer was extracted with ether, and the oil and extract were combined, washed with water, and dried over calcium chloride. Fractionation gave 27.1 g (82%) of a mixture of mononitropropylbenzenes, b.p. 112-120° (8 mm), and 5.9 g of unchanged propylbenzene was recovered; the residue amounted to 0.6 g.

b) Under analogous conditions 33.5 g of butylbenzene gave 30 g (89%) of a mixture of mononitrobutylbenzenes, b.p. 107-115° (4 mm), and 8.3 g of unchanged butylbenzene was recovered; the residue amounted to 0.9 g.

c) Under the same conditions 33.5 g of isobutylbenzene gave 33.3 g (94%) of a mixture of mononitroisobutylbenzenes, b.p. 100-108° (4 mm), and 7.1 g of unchanged isobutylbenzene was recovered; residue 0.4 g.

Oxidation of Mononitro Compounds with Chromium Trioxide.

a) A mixture of 2.0 g of the mixture of mononitropropylbenzenes, 13 g of chromium trioxide, 30 ml of water, 30 ml of acetic acid, and 10 ml of concentrated sulfuric acid was refluxed until exothermic oxidation set in. When heat ceased to be evolved, the reaction mixture was boiled further for one hour. Cooling, filtering, and drying gave 0.8 g (39.6%) of p-nitrobenzoic acid, m.p. 237-239°, undepressed by admixture of a known sample. A repeat experiment gave 0.78 g of p-nitrobenzoic acid. It follows from a comparison of the result with data on the oxidation of pure p-nitrotoluene [6] that nitration of propylbenzene gives a mixture of mononitropropylbenzenes containing 44% of p-isomer and 56% of o-isomer.

b) Oxidation under analogous conditions of 2.0 g of the mixture of mononitrobutylbenzenes gave 0.72 g (38.7%) of p-nitrobenzoic acid, m.p. 237-239°, undepressed by admixture of a known sample; this corresponds to a mixture of 43% of p-isomer and 57% of o-isomer. A repeat experiment gave 0.71 g of p-nitrobenzoic acid.

c) Oxidation under the same conditions of 2.0 g of the mixture of mononitroisobutylbenzenes gave 0.71 g (38.2%) of p-nitrobenzoic acid, m.p. 237-239°, undepressed by admixture of a known sample; this corresponds almost exactly to the composition of the mixture of mononitrobutylbenzenes, i.e. 43% of p-isomer and 57% of o-isomer. A repeat experiment gave 0.70 g of p-nitrobenzoic acid.

SUMMARY

1. It was shown that the chloromethylation of propyl-, butyl-, and isobutyl-benzenes and cyclohexylbenzene results in the formation of mixtures of o- and p-(chloromethyl) derivatives.

2. A comparison was made between the ortho-para ratios obtained in the chloromethylation of alkylbenzenes and the analogous data for nitration.

3. The observed facts were explained on the basis of steric interactions occurring in these electrophilic aromatic substitutions (steric factor).

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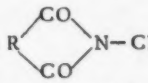
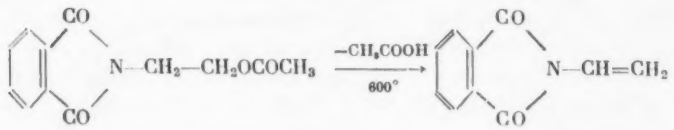
POLYMERIZATION AND COPOLYMERIZATION OF N-VINYL COMPOUNDS

COMMUNICATION 3. SYNTHESIS OF THE VINYLIMIDES OF SUCCINIC, PHTHALIC, AND NAPHTHALIC ACIDS

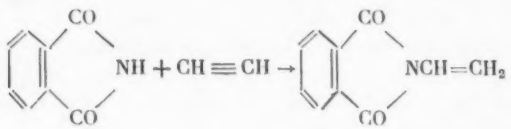
A. F. Nikolaev and S. N. Ushakov

Vinylimides of general formula  have recently begun to interest investigators owing to the possibility of using them in the synthesis of macromolecular polymers having high softening point (above 200°) and other technically valuable properties. As yet, only N-vinylphthalimide has been studied. After the publication, in 1942, of an accessible synthesis by the pyrolysis of N-2-acetoxyethylphthalimide [1], some papers [2,3] and patents appeared on its polymerization and on its copolymerization with various unsaturated compounds, namely, maleic anhydride [5], ethylene [6], propene [7], and vinyl acetate [8]. The synthesis of N-vinylphthalimide can be effected by two methods:

1. Pyrolysis of N-2-acetoxyethylphthalimide [1,9] at 560-600°:



2. Addition of acetylene to phthalimide in presence of mercury [10] or cadmium [11] salts:

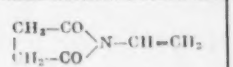
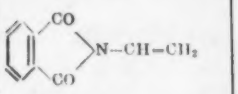
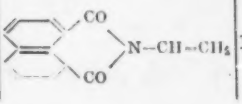


We synthesized N-vinylphthalimide in three stages: 1) preparation of N-2-ethoxyethylphthalimide from phthalic anhydride and 2-aminoethanol [12,13]; 2) preparation of N-2-acetoxyethylphthalimide by reaction of N-2-hydroethylphthalimide with acetic anhydride; 3) preparation of N-vinylphthalimide by pyrolysis of N-2-acetoxyethylphthalimide according to the above scheme. In a similar way we synthesized two other vinylimides, namely N-vinylsuccinimide and N-vinylnaphthalimide. We did not succeed in finding information on the synthesis of N-vinylsuccinimide in the scientific literature, and the patent references [4] give no information on this matter. We are the first to synthesize N-vinylnaphthalimide. The properties of the N-vinyl compounds obtained are given in the Table.

The vinylimides of succinic, phthalic, and naphthalic acids are soluble in alcohols, ketones, esters, aromatic and halogen-substituted hydrocarbons, organic acids, and amines. N-Vinylsuccinimide is soluble also in water. They may be analyzed by bromination methods and by Kjeldahl or Dumas nitrogen determination. The monomers readily polymerize and readily copolymerize with other unsaturated compounds in presence of initiators.

TABLE

Properties of Vinylimides

No.	Vinylimide	Formula		B.p. in °C (p_{mm})	Bromine value		Nitrogen content	
					calculated	found	calculated	found
1	N-Vinylsuccinimide		48.5	100(3)	127.75	127.34	11.20	11.15
2	N-Vinylphthalimide		83.0	140(2)	92.31	91.95	8.09	8.07
3	N-Vinylnaphthalimide		126.0	174(5)	71.61	71.01	6.28	6.20

Homopolymers of vinylimides have high softening points (230-240°), are transparent, and are of limited solubility. Products having various properties can be obtained by copolymerization with vinyl acetate, methyl methacrylate, and styrene.

EXPERIMENTAL

N-2-Hydroxyethylphthalimide. Freshly distilled 2-aminoethanol (60 ml, i.e. 61 g, i.e. 1 mole) was added gradually (with avoidance of overheating and foaming of the reaction mixture) to 148 g (1 mole) of phthalic anhydride in a 500-ml round-bottomed flask. The mixture was heated for 60-90 minutes in a sand (or air) bath at 140° (the thermometer was immersed in the reaction mixture). When reaction was complete (cessation of liberation of water vapor), the N-2-hydroxyethylphthalimide was recrystallized from 500 ml of boiling distilled water and dried, first at room temperature and then in a drying cupboard at 70-90°, to constant weight. The yield of colorless crystals, m.p. 127°, was 187-189 g (98-99%).

N-2-Acetoxyethylphthalimide. A mixture of 191 g (1 mole) of N-2-hydroxyethylphthalimide and 189 ml (204 g, i.e. 2 moles) of acetic anhydride was prepared in a 1-liter round-bottomed flask fitted with reflux condenser. The mixture was kept at a gentle boil on a sand bath for five hours. When reaction was complete, the hot brown solution was poured with stirring into distilled water. The yellowish precipitate of N-2-acetoxyethylphthalimide was filtered off, washed with water, and dried to constant weight in a drying cupboard at 50-60°. The yield was 223-226 g (96-98%). After recrystallization from hot water, N-2-acetoxyethylphthalimide was obtained in colorless crystals, m.p. 90°.

N-Vinylphthalimide. Fused N-2-acetoxyethylphthalimide was dropped from a dropping funnel at the rate of 30 drops per minute into a hot (600°) quartz or porcelain tube, diameter 20 mm and length not less than 400 mm, inclined at an angle of 25°. The pyrolysis products were collected in a two-necked flask attached to the end of the pyrolysis tube and having an air condenser. The dark-brown condensate, which consisted of a mixture of N-vinylphthalimide, unchanged N-2-acetoxyethylphthalimide, acetic acid, and decomposition products, was vacuum-fractionated. The first runnings were acetic acid, boiling up to 50° (60 mm), and then, at 130-160° (3 mm), N-vinylphthalimide came over and solidified in the flask as a yellow crystalline mass. After two recrystallizations from methanol, N-vinylphthalimide was obtained as a white crystalline powder, m.p. 83° and b.p. 140° (2 mm). At this stage the yield of N-vinylphthalimide attained 85-90%.

Sokolova [9] synthesized N-vinylphthalimide in six stages with an overall yield of 25%. In the pyrolysis of N-2-acetoxyethylphthalimide the yield of N-vinylphthalimide was about 90%.

N-Vinylphthalimide was analyzed for nitrogen by the semimicro Kjeldahl method and for the double bond by Kaufmann's method. The analytical results are given in the Table.

N-2-Hydroxyethylsuccinimide. Anhydrous 2-aminoethanol (60 ml, i.e. 61 g, i.e. 1 mole) was added gradually to 118 g (1 mole) of succinic acid in a 500-ml round-bottomed flask. The mixture was heated for 60-90 minutes at 160° in an air bath. After the liberation of water vapor had ceased and the product had cooled, the N-2-hydroxyethylsuccinimide solidified to a light-yellow crystalline mass. After being vacuum-distilled at 178° (5 mm) and recrystallized from boiling benzene, N-2-hydroxyethylsuccinimide was obtained as a white crystalline powder, m.p. 58°. The yield was 95%.

N-2-Acetoxyethylsuccinimide. The procedure was similar to that for N-2-acetoxyethylphthalimide. When the process was complete, the reaction mixture was vacuum-fractionated. Acetic acid and acetic anhydride came over up to 70° (50 mm), and then at 142-145° (3 mm) N-2-acetoxyethylsuccinimide came over as a colorless viscous liquid; d_4^{20} 1.2410; n_D^{20} 1.4810; yield 95%.

N-Vinylsuccinimide. This was prepared by the pyrolysis of N-2-acetoxyethylsuccinimide, the procedure being similar to that for N-vinylphthalimide. From the dark-brown condensate N-vinylsuccinimide came over in the range 100-130° (3 mm) and solidified in the flask to a light-yellow mass. It was purified by two crystallizations from warm distilled water. Pure N-vinylsuccinimide is a white crystalline substance, m.p. 48.5°, b.p. 100° (3 mm); n_D^{20} 1.5020; yield 85-90%.

N-2-Hydroxyethylnaphthalimide. This was synthesized from naphthalic anhydride and 2-aminoethanol by the described procedure [14]. The yield of yellowish crystalline product, m.p. 171°, was 98%. The naphthalic anhydride was prepared by the oxidation of acenaphthene by the procedure described by Kipriyanov and Dashevsky [15].

N-2-Acetoxyethylnaphthalimide. According to the literature this can be prepared by the action of acetyl chloride on N-2-hydroxyethylnaphthalimide [16]; however, we synthesized it by the procedure used for N-2-acetoxyethylphthalimide. When the dark-brown solution was cooled, N-2-acetoxyethylnaphthalimide, m.p. 134°, crystallized out; yield 85%.

N-Vinylnaphthalimide. A hot solution of N-2-acetoxyethylnaphthalimide in acetic acid was dropped from a dropping funnel into the pyrolysis tube, which was heated to 650°, at 30-40 drops per minute (at a lower temperature no elimination of acetic acid was observed). The condensate was vacuum-distilled; N-vinylnaphthalimide was collected over the range 160-180° (5 mm).

When recrystallized from methanol, N-vinylphthalimide melted at 126° and boiled at 174° (5 mm). The yield was 20%. The analytical results are given in the Table.

SUMMARY

1. The conditions required in the preparation of N-vinylphthalimide and N-vinylsuccinimide were defined more precisely, and the yields obtained were improved considerably.

2. N-Vinylnaphthalimide was synthesized for the first time and its properties were determined. The scheme of synthesis was naphthalic anhydride → N-2-hydroxyethylnaphthalimide → N-2-acetoxyethylnaphthalimide → N-vinylnaphthalimide.

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CONDENSATION OF BENZALDEHYDE DIETHYL ACETAL WITH ETHYL VINYL ETHER

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In 1939 Meuller-Cunradi and Pieroh [1] reported in a patent that in presence of an acid catalyst acetaldehyde diethyl acetal adds to ethyl vinyl ether with formation of 1,1,3-triethoxybutane (I):

$$CH_3 - CH(OC_2H_5)_2 + CH_2 = CHOC_2H_5 \rightarrow CH_3 - CH(OC_2H_5) - CH_2 - CH(OC_2H_5)_2 \qquad (I)$$

In its turn the ethoxy acetal (I) can condense with ethyl vinyl ether with formation of 1,1,3,5-tetraethoxyhexane, which can enter into further condensation.

Later, Hoaglin and Hirsch [2] showed that this reaction is given by various aliphatic acetals and α,β-unsaturated ethers. For several cases these authors studied the effect of various factors on the course of the reaction and established its mechanism. The reaction of acetals with α,β-unsaturated ethers can proceed either through the splitting off of α-hydrogen, as Meuller-Cunradi and Pieroh supposed, or by the splitting off of an alkoxy group of the acetal with addition of the fragments formed to the double bond of the unsaturated ether. These two mechanisms may be represented as follows:

1. $$H \ldots CH(R^1) - CH(OR^3)_2 + R^2 - CH = CHOR^3 \rightarrow$$

$$\rightarrow R^2 - CH_2 - CH(OR^3) - CH(R^1) - CH(OR^3)_2$$

2. $$R^1 - CH_2 - CH\langle_{OR^3}^{OR^3} + R^2 - CH = CH - OR^3 \rightarrow$$

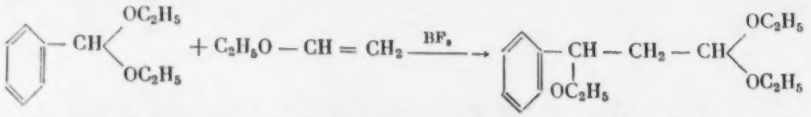
$$\rightarrow R^1 - CH_2 - CH(OR^3) - CH(R^2) - CH\langle_{OR^3}^{OR^3}$$

The structure of the product will depend on the mechanism of the reaction.

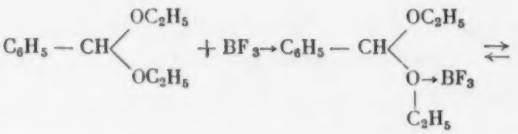
Hoaglin and Hirsch showed that the second mechanism is correct. They showed also that, in order to obtain a high yield of primary-condensation products (60-70%), reaction should be carried out in presence of a large excess (3-5-fold) of the acetal. With a smaller excess of the acetal the formation of a considerable amount of further condensation products is observed and the yield of primary condensation products is less. The catalyst used was the ether complex of boron trifluoride, and it was shown that zinc chloride can also be used. Shostakovsky and Gladyshevskaya [3,4] found that the condensation of acetals with vinyl ethers proceeds also in presence of ferric chloride.

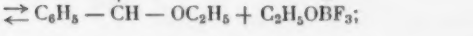
Acetals can react not only with α,β-unsaturated ethers, but also with other compounds containing an activated double bond, such as dihydropyran and dihydrofuran [5]. On the other hand, α,β-unsaturated ethers can condense not only with acetals, but also with ketals, an example of which is the synthesis of vitamin A from β-ionone [6].

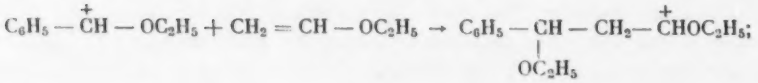
The condensation of benzaldehyde dimethyl acetal with methyl vinyl ether was described in a patent by Copenhaver [7]. In the present investigation we studied the condensation of benzaldehyde diethyl acetal with ethyl vinyl ether in presence of boron trifluoride. It was shown that reaction proceeds with formation of (1,3,3-triethoxypropyl)benzene (I) in accordance with the equation:

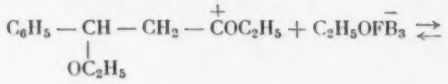


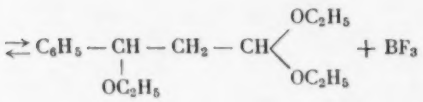
The realization of this reaction is clear confirmation of the correctness of the second mechanism of the condensation, proposed by Hoaglin and Hirsch, since reaction in accordance with the first mechanism is excluded here. It may be supposed that boron trifluoride acts in the following way:





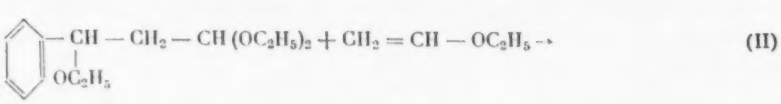


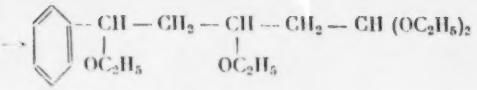




The condensation of benzaldehyde diethyl acetal with the vinyl ether differs substantially from the analogous reaction of acetals of the aliphatic series. As indicated above, in the condensation of aliphatic acetals with α,β-unsaturated ethers a large excess of acetal is necessary for the production of the primary product in high yield. This is to be explained by the fact that there is only a small difference in the rates with which the original acetal and the ethoxy acetal formed by the addition of one molecule of unsaturated ether condense with this ether. In the case of the benzaldehyde acetal, however, the addition of one molecule of vinyl ether results in the formation of an ethoxy acetal of the aliphatic-aromatic series. In aromatic acetals the alkoxy radical is more mobile than in acetals of the aliphatic-aromatic series, so that the rate of condensation of the benzaldehyde acetal with the vinyl ether is much higher than the rate of condensation of (1,3,3-triethoxypropyl)benzene. This makes it possible to obtain a yield of (1,3,3-triethoxypropyl)benzene of about 70% even though the molar ratio of benzaldehyde acetal and vinyl ether is 1 : 1.

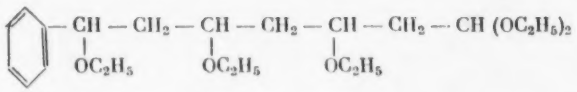
Experiments on the condensation of (1,3,3-triethoxypropyl)benzene with ethyl vinyl ether showed that, in order to obtain a high yield of primary-condensation product in this case, a large excess of the acetal must be used. With a three-fold excess the primary-condensation product (1,3,5,5-tetraethoxypentyl)benzene (II) was obtained in a yield of 50% on the amount of vinyl ether taken:

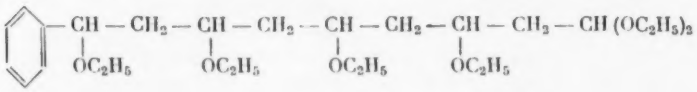




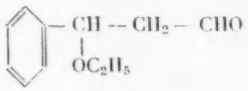
With a molar ratio of 1 : 1 the yield of (II) was not above 10% and at the same time a large amount of further-condensation products was formed. It will be clear that both the original (1,3,3-triethoxypropyl) - benzene and products of its condensation with one or more molecules of vinyl ether are ethoxy acetals of the aliphatic-aromatic series, which differ very little in their rates of condensation with the vinyl ether. As in the case of the reaction of aliphatic acetals with α,β-unsaturated ethers, these circumstances make it necessary to have a large excess of the acetal in order to ensure a high yield of primary condensation product and suppression of the formation of further condensation products.

In the condensation of (1,3,3-triethoxypropyl)benzene with ethyl vinyl ether at a molar ratio of about 1 : 1, together with the primary-condensation product (1,3,5,5-tetraethoxypentyl)benzene we obtained a considerable amount of products of the addition of two and more ether molecules to the original ethoxy acetal. From these we succeeded in isolating individual compounds corresponding to the addition of three and four molecules of ethyl vinyl ether to the benzaldehyde acetal, namely, (1,3,5,7,7-pentaethoxyheptyl)benzene [1,1,3,5,7-pentaethoxy-7-phenylheptane] (III) and (1,3,5,7,9,9-hexaethoxynonyl)benzene [1,1,3,5,7,9-hexaethoxy-9-phenylnonane] (IV):

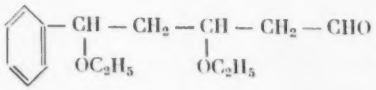




These compounds are undoubtedly of some preparative interest. In order to carry out further transformations we studied ways of converting the ethoxy acetals that we had obtained into the corresponding ethoxy aldehydes. We found that the acetal groups were readily hydrolyzed by boiling dilute hydrochloric acid. We isolated the following two previously undescribed aldehydes:



β-ethoxyhydrocinnamaldehyde (V) and



3,5-diethoxy-5-phenylvaleraldehyde (VI).

Longer boiling of the original ethoxy acetals with hydrochloric acid resulted in the elimination of alcohol with formation of phenylated polyenic aldehydes.

EXPERIMENTAL

Benzaldehyde diethyl acetal was prepared by the action of ethanol on benzaldehyde in presence of HCl [8] and had b.p. 216-219° (760 mm); d_4^{20} 0.9699, n_D^{20} 1.4822. The vinyl ether was washed with water, dried over potassium carbonate, and distilled over sodium; b.p. 36-36.5°; n_D^{20} 3776.

Condensation of Benzaldehyde Diethyl Acetal with Ethyl Vinyl Ether (1,3,3-Triethoxypropyl)benzene. To 140 g (0.78 mole) of benzaldehyde diethyl acetal, 0.28 g of an ethereal solution of boron trifluoride etherate containing 25% of BF_3 was added. The solution was heated to 49° and vigorously stirred while 50 g (0.69 mole) of ethyl vinyl ether was added at such a rate that the temperature could be maintained at 48-50° when the reaction mixture was cooled with water. When addition was complete, the reaction mixture was stirred for 15 minutes and cooled to room temperature. In order to neutralize the catalyst, 1.5 g of anhydrous sodium carbonate powder was added and the mixture was stirred for three hours. The precipitate was filtered off, and the product was vacuum-fractionated in presence of a little anhydrous sodium carbonate.

The following fractions were obtained: Fraction I, 88-90° (7 mm), 40 g; fraction II, 90-128° (7 mm), 4.5 g; fraction III, 128-130° (7 mm), 125 g; residue 15 g.

The first fraction was unchanged benzaldehyde acetal. The 128-130° fraction corresponded to (1,3,3-triethoxypropyl)benzene (yield 71.9% on the vinyl ether), and after redistillation it had the following properties: b.p. 130-131° (7 mm) and 97-98° (2 mm); d_4^{20} 0.9642; n_D^{20} 1.4724; found MR 73.34; calculated MR 72.70.

Found %: C 71.40, 71.34; H 9.56, 9.40. $C_{15}H_{24}O_3$.

Calculated %: C 71.39; H 9.59.

In the fractionation of the residue obtained in this experiment we isolated 4.5 g (4% on the vinyl ether) of (1,3,5,5-tetraethoxypentyl)benzene, b.p. 167-169° (7 mm), d_4^{20} 0.9659; n_D^{20} 1.4703; found MR 93.49; calculated MR 91.81.

Condensation of (1,3,3-Triethoxypropyl)benzene with Ethyl Vinyl Ether (1,3,5,5-Tetraethoxypentyl)-benzene. To 85 g (0.34 mole) of (1,3,3-triethoxypropyl)benzene, 0.17 g of a 25% solution of BF_3 in ether was added. The mixture was heated to 49°, and 8 g (0.11 mole) of ethyl vinyl ether was added. When addition was complete, the mixture was stirred further for 15 minutes. The catalyst was neutralized by stirring the reaction mixture with 1 g of anhydrous sodium carbonate for three hours at 50°. The precipitate was filtered off, and the product was vacuum-fractionated. The following fractions were obtained: Fraction I, 100-102° (2.5 mm), 54.5 g; Fraction II, 102-137° (2.5 mm), 7.5 g; Fraction III, 137-140° (2.5 mm), 17.5 g; residue 9 g.

Fraction I corresponded to the original (1,3,3-triethoxypropyl)benzene. Redistillation of Fraction III gave (1,3,5,5-tetraethoxypentyl)benzene (yield 50% on the vinyl ether), b.p. 123-124° (2 mm); d_4^{20} 0.9666, n_D^{20} 1.4698; found MR 93.32; calculated MR 91.81

Found %: C 70.66, 70.58; H 9.81, 9.89. $C_{19}H_{31}O_4$.

Calculated %: C 70.55; H 9.66.

Fraction II probably consisted of a mixture of (1,3,3-triethoxypropyl)benzene and (1,3,5,5-tetraethoxypentyl)benzene, but it was extremely difficult to separate by fractionation. In the condensation of (1,3,3-triethoxypropyl)benzene with ethyl vinyl ether at a molar ratio of 1 : 1, the yield of (1,3,5,5-tetraethoxypentyl)-benzene was 10% on the vinyl ether taken. In addition we obtained a large residue of b.p. above 140° (2.5 mm). By repeated fractionation of 100 g of this residue we isolated two more substances:

1) a substance (28 g) of b.p. 156-158° (2 mm) corresponding in analysis to (1,3,5,7,7-pentaethoxyheptyl) benzene; d_4^{20} 0.9682; n_D^{20} 1.4682; found MR 113.83; calculated MR 113.03.

Found %: C 69.70, 69.87; H 10.02, 10.01. $C_{23}H_{40}O_5$.

Calculated %: C 69.66; H 10.17.

2) a substance (15 g) of b.p. 180-182° (2 mm) corresponding in analysis to (1,3,5,7,9,9-hexaethoxynonyl)benzene; d_4^{20} 0.9688, n_D^{20} 1.4670; found MR 134.3; calculated MR 133.16.

Found %: C 69.38, 69.33; H 10.14, 10.18. $C_{27}H_{48}O_6$.

Calculated %: C 69.19; H 10.32.

Hydrolysis of (1,3,3-Triethoxypropyl)benzene β-Ethoxyhydrocinnamaldehyde. Aqueous 2% hydrochloric acid (60 ml) was added to 58 g of (1,3,3-triethoxypropyl)benzene, and the mixture was heated to boiling under a fractionation column. After 5-10 minutes the temperature in the vapor fell to 78°, and the alcohol that separated was distilled off until the temperature again began to rise; 21 g of ethanol was distilled off. The reaction mixture was extracted with ether, and the extract was washed free from HCl with water, dried over calcium chloride, and vacuum-distilled with an addition of sodium acetate. The product, amounting to 36 g (88%), was β-ethoxyhydrocinnamaldehyde, b.p. 80-81° (2 mm), d_4^{20} 1.0210; n_D^{20} 1.5087, found MR 52.09, calculated MR 51.05.

Found %: C 74.07, 73.92; H 7.76, 7.63. $C_{11}H_{14}O_2$.

Calculated %: C 74.13; H 7.92.

Hydrolysis of (1,3,5,5-Tetraethoxypentyl)benzene 3,5-Diethoxy-5-phenylvaleraldehyde. A mixture of 26 g of (1,3,5,5-tetraethoxypentyl)benzene and 40 ml of 2% hydrochloric acid was boiled with removal of alcohol formed through a column until the temperature began to rise above 77°. The product was isolated as in the preceding experiment. The product, amounting to 15 g (75 %), was 3,5-diethoxy-5-phenylvaleraldehyde, b.p. 111-112° (2 mm); d_4^{20} 1.0060, n_D^{20} 1.4950; found MR 72.56, calculated MR 71.17.

Found %: C 72.10, 71.86; H 8.81, 8.69. $C_{15}H_{22}O_3$.

Calculated %: C 71.97; H 8.86.

SUMMARY

1. A study was made of the condensation of benzaldehyde diethyl acetal with ethyl vinyl ether.

2. It was shown that in this reaction aliphatic-aromatic ethoxy acetals of general formula C_6H_5-$(CHOC_2H_5-CH_2)_nCH(OC_2H_5)_2$ are formed.

3. By the hydrolysis of these ethoxy acetals, aliphatic-aromatic ethoxy aldehydes were prepared.

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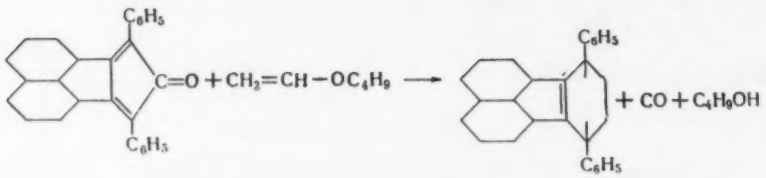
VINYL COMPOUNDS IN THE DIENE SYNTHESIS

COMMUNICATION 1. REACTIONS OF SOME VINYL ETHERS WITH CYCLOPENTADIENE AND WITH HEXACHLOROCYCLOPENTADIENE

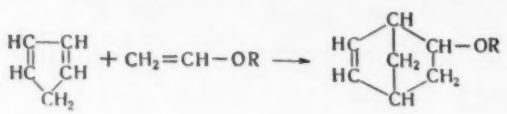
M. F. Shostakovsky, A. V. Bogdanova, and T. M. Ushakova

The desirability of continuing our systematic study of vinyl ethers and the alluring prospect of preparing interesting compounds from them prompted us to investigate the conditions of the diene synthesis, in which vinyl ethers can take part as dienophilic components. The behavior of vinyl esters and other unsaturated compounds in the diene synthesis was studied by Alder [1], Diels [2], and Petrov [3]. On the behavior of vinyl ethers there have been only isolated investigations [4,5], in which it was shown that the use of certain vinyl ethers in the diene condensation is possible in principle. However, in these investigations the subject of study was the dienes used rather than the vinyl ethers, which were brought into the picture in a somewhat casual fashion. In one of these investigations Plate and Meerovich [4] isolated the adduct formed by butyl vinyl ether with cyclopentadiene (I) and hydrogenated it to 2-butoxybicyclo(2,2,1)heptane. Abramov and Tsyplenkova [5] studied the reaction of butyl vinyl and phenyl vinyl ethers with certain cyclic ketones, which proceeded as follows:



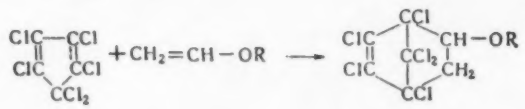
(a)

Meek and Trapp [6], in a study of the Diels-Alder reactions of chloroprene, used ethyl vinyl ether as one of the dienophiles, but did not succeed in obtaining the desired adduct. The present investigation forms the beginning of a systematic study of the behavior of various vinyl ethers in the diene condensation with various dienes. A study was made of the conditions of reaction of butyl vinyl, cyclohexyl vinyl, and phenyl vinyl ethers with cyclopentadiene and hexachlorocyclopentadiene; these reactions proceed as follows:



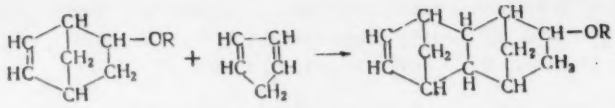
(b)

in which R = C_4H_9 (I), C_6H_5 (II), C_6H_{11} (III);



(c)

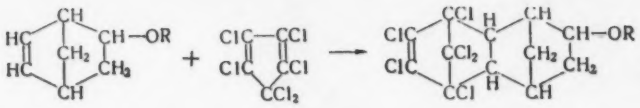
in which R = C_4H_9, C_6H_5 (IIIa); they are stepwise in character, for the bicycloheptenyl ether will react with a second molecule of cyclopentadiene and give an octahydro-1,4,5,8-dimethanonaphthyl ether (IV, V, VI):



(d)

in which R = C_4H_9 (IV), C_6H_5 (V), C_6H_{11} (VI).

Such products were isolated from the high-boiling fractions; they contained two cyclopentadiene units in the molecule. The yields of these were increased by increase in the amount of diene in the original mixture and, correspondingly, the yields of the main adducts were increased by increase in the amount of vinyl ether. The stepwise character of this reaction makes it possible to carry out the second stage (d) with other dienes, such as hexachlorocyclopentadiene, which gives ethers of the hexachlorooctahydro-1,4,5,8-dimethanonaphthalene series (VII, VIII), which are of interest from the point of view of their possible insecticidal activity:

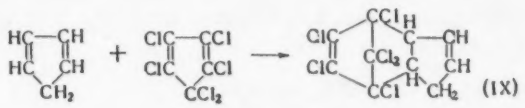


(e)

in which R = C_4H_9 (VII), C_6H_5 (VIII).

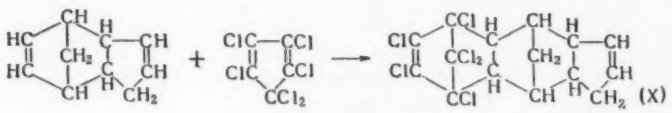
In the reaction of vinyl ethers with cyclopentadiene, the main reaction is accompanied by the formation of an undistillable residue consisting mainly of a copolymer of the vinyl ether and cyclopentadiene.

It is known that cyclopentadiene [7] and cyclopentene [8] react with hexachlorocyclopentadiene with formation of adducts (IX) of the tetrahydro-4,7-methanoindene series:



(f)

This reaction can be carried out similarly with cyclopentadiene dimer; it proceeds smoothly and gives a compound containing five five-membered rings in its molecule (X):



(g)

As Volfson, Melnikov, Plate, and co-workers have shown [8], products such as this are fairly stable and have insecticidal properties.

EXPERIMENTAL

Starting Materials. Butyl vinyl ether, b.p. 93-94° and n_D^{20} 1.4030. Cyclohexyl vinyl ether, b.p. 64--64.5° (34 mm), n_D^{20} 1.4540. Phenyl vinyl ether, b.p. 156-156.5°, and n_D^{20} 1.5228. Cyclopentadiene, b.p. 40--41° and n_D^{20} 1.4446. Cyclopentadiene dimer, b.p. 56-57° (13 mm) and n_D^{20} 1.5126. Hexachlorocyclopentadiene, b.p. 104.5-105° (10 mm) and n_D^{20} 1.5638.

1. Reaction of Butyl Vinyl Ether with Cyclopentadiene: Preparation of 5-Butoxybicyclo [2,2,1]hept--2-ene (I) and 2-Butoxy-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethanonaphthalene (IV). A mixture of 18.8 g of cyclopentadiene dimer and 72 g of butyl vinyl ether (1 : 2) was heated in a rotating autoclave at 190-200°

for 14 hours. Excess of butyl vinyl ether was distilled off. Vacuum fractionation of the residue gave: Fraction I, 75-120° (13 mm), 15.0 g; Fraction II, 120-160° (10 mm), 17.5 g; residue 20.5 g.

After being freed from dibutyl acetal [4], Fraction I consisted of 5-butoxybicyclo 2 2 1 hept-2- ene(I), b.p. 46-47° (2 mm), n_D^{20} 1.4621; d_4^{20} 0.9189; found MR 50.12; for $C_{11}H_{18}O$, calculated MR 49.80; yield 31.9%. The literature [4] gives: b.p. 67-68° (6 mm), n_D^{20} 1.4662, d_4^{20} 0.9247.

After two distillations Fraction II gave 2-butoxy-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethanonaphthalene (IV), b.p. 119-120° (3 mm); n_D^{20} 1.4948; d_4^{20} 0.9927; found MR 68.14, $C_{16}H_{24}O$; calculated MR 68.49.

Found %: C 82.50, 82.27; H 10.69, 10.56. $C_{16}H_{24}O$.

Calculated %: C 82.70; H 10.41.

Found M: 223.2, 226.5. $C_{16}H_{24}O$.

Calculated M: 232.3.

The resinous residue, a colored transparent mass, was precipitated from ethereal solution with methanol and was then isolated as a solid polymer. After being vacuum-dried at 60° it had the following composition:

Found %: C 81.68, 81.54; H 9.64, 9.60.

Found M: 710.3.

This product was a copolymer of butyl vinyl ether and cyclopentadiene and, according to elementary analysis, consisted of 38.68 moles % of butyl vinyl ether and 61.32 moles % of cyclopentadiene.

2. Reaction of Phenyl Vinyl Ether with Cyclopentadiene: Preparation of 5-Phenoxybicyclo 2 2 1 hept--2-ene (II) and 1,2,3,4,4a,5,8,8a-2-phenoxy-1,4,5,8-dimethanonaphthalene (V). Reaction, as in the previous experiment, between 9 g of cyclopentadiene dimer and 36 g of phenyl vinyl ether (1 : 2) at 200° for 15 hours gave a mixture from which excess of the vinyl ether was then removed. Vacuum fractionation gave: Fraction I, 100-140° (6 mm), 17.8 g; Fraction II, 140-180° (6 mm), 7.2 g; residue 1.7 g.

From Fraction I we isolated 5-phenoxybicyclo 2 2 1 hept-2-ene (II), a colorless viscous liquid of camphor odor having the following constants: b.p. 114-114.5° (5 mm); n_D^{20} 1.5500; d_4^{20} 1.0732; found MR 55.31, $C_{13}H_{14}O$ for , calculated MR 55.41.

Found %: C 84.22, 84.15; H 7.80, 7.70. $C_{13}H_{14}O$.

Calculated %: C 84.36; H 7.58.

Found M: 188.8, 186.8. $C_{13}H_{14}O$.

Calculated M: 186.3

The yield of (II) was 70.1%.

From Fraction II we isolated 1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethanonaphthalene (V), a clear yellowish balsamlike substance, b.p. 172-173° (4 mm).

Found %: C 84.89, 85.11; H 7.81, 7.93. $C_{18}H_{20}O$.

Calculated %: C 85.66; H 7.99.

Found M: 275.7, 269.8. $C_{18}H_{20}O$.

Calculated M: 252.4.

Reprecipitation of the residue gave 0.9 g of a copolymer of phenyl vinyl ether and cyclopentadiene as a white powder which softened at 140-150°.

Found %: C 83.01, 83.22; H 7.81, 7.83.

Found M: 837.5.

This substance had the composition (moles %): phenyl vinyl ether 52.9, cyclopentadiene 47.1. The yield of copolymer was 2% on the original mixture.

In a similar way, from cyclohexyl vinyl ether and cyclopentadiene taken in the proportions of 2 : 1 we obtained 5-(cyclohexyloxy)bicyclo[2.2.1]hept-2-ene (III), which had the following constants: b.p. 105--107° (4 mm); n_D^{20} 1.4882; d_4^{20} 0.9759; found MR 57.11; $C_{13}H_{21}O$. Calculated MR 57.91.

Found %: C 79.76, 79.62; H 10.73, 10.71. $C_{13}H_{21}O$.

Calculated %: C 80.74; H 10.95.

The yield of 5-(cyclohexyloxy)bicyclo[2.2.1]hept-2-ene was 52.8%. When the reactants were in the proportions of 1 : 1 we isolated 2-(cyclohexyloxy)-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethanonaphthalene (VI), b.p. 111-112° (2 mm); n_D^{20} 1.5070; d_4^{20} 1.0122; found MR 76.28; $C_{18}H_{27}O$. Calculated MR 76.60; yield 21%.

Found %: C 83.54, 83.41; H 10.32, 10.20. $C_{18}H_{27}O$.

Calculated %: C 83.35; H 10.49.

3. Reaction of Phenyl Vinyl Ether with Hexachlorocyclopentadiene: Preparation of 1,2,3,4,7,7--Hexachloro-5-phenoxybicyclo[2.2.1]hept-2-ene (IIIa). A mixture of 2.4 g of phenyl vinyl ether, 5.46 g of hexachlorocyclopentadiene, and 0.2 g of hydroquinone was heated at 120-130° under reflux for two hours. Vacuum fractionation of the reaction mixture gave 2.3 g of hexachlorocyclopentadiene and 5.6 g of 1,2,3,4,-7,7-hexachloro-5-phenoxybicyclo[2.2.1]hept-2-ene (IIIa), b.p. 172-172.5° (1 mm), yield 72.0%.

Found %: C 40.55, 40.46; H 2.26, 2.17; Cl 53.35, 53.43. $C_{13}H_8OCl_6$.

Calculated %: C 39.78; H 2.05; Cl 54.11.

4. Reaction of 5-Butoxybicyclo[2.2.1]hept-2-ene (I) with Hexachlorocyclopentadiene (1 : 1): Preparation of 2-Butoxy-5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethanonaphthalene * (VII). A mixture of 3.4 g of 5-butoxybicyclo[2.2.1]hept-2-ene (I) and 5.4 g of hexachlorocyclopentadiene was heated at 125-130° under reflux for three hours. Vacuum distillation of the colored sirupy product gave 4.0 g (44%) of the butoxyhexachlorooctahydro-1,4,5,8-dimethanonaphthalene (VII), a sirupy, almost colorless liquid of b.p. 198-198.5° (2 mm).

Found %: C 44.20, 44.02; H 4.07, 4.07; Cl 48.09, 48.38. $C_{16}H_{18}OCl_6$.

Calculated %: C 44.78; H 4.13; Cl 48.46.

5. Reaction of 5-Phenoxybicyclo[2.2.1]hept-2-ene (II) with Hexachlorocyclopentadiene: Preparation of 5,6,7,8,9,9-Hexachloro-1,2,3,4,4a,5,8,8a-octahydro-2-phenoxy-1,4,5,8-dimethanonaphthalene (VIII). Under the same conditions 1.9 g of 5-phenoxybicyclo[2.2.1]hept-2-ene (II) and 2.7 g of hexachlorocyclopentadiene gave 2.0 g of unchanged reactants and 2.48 g of the hexachlorooctahydrophenoxy-1,4,5,8-dimethanonaphthalene (VIII), b.p. 225-227° (2 mm), yield 96.2%. We did not succeed in obtaining a purer product under the conditions of vacuum distillation.

Found %: C 47.73, 47.57; H 3.18, 3.26; Cl 44.72, 44.96. $C_{18}H_{14}OCl_6$.

Calculated %: C 47.10; H 3.07; Cl 46.34.

6. Reaction of Cyclopentadiene and its Dimer with Hexachlorocyclopentadiene: Preparation of 4,5,6,7,8,8-Hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (IX) and 5,6,7,8,10,10-Hexachloro-3a,4,4a-5,8,8a,9,9a-octahydro-4,9,5,8-dimethano-1H-benz[f]indene (X). A mixture of equimolecular amounts of the reactants was heated at 135-140° under reflux for one hour. The crystalline products obtained were purified by recrystallization.

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*Chemical Abstracts numbering of this is 6—1,2,3,4,10,10—1,4,4a,5,6,7,8,8a—1,4,5,8, but numbering initiated in the saturated ring is retained in (VII) and (VIII) to maintain uniformity with (IV), (V), and (VI) - Publisher.

The hexachlorotetrahydro-4,7-methanoindene (IX) had m.p. 153-154° (from methanol).

Found %: C 35.67, 35.64; H 1.71, 1.69; Cl 62.81, 62.83. $C_{10}H_6Cl_6$.

Calculated %: C 35.44; H 1.77; Cl 62.79.

The hexachlorooctahydro-4,9,5,8-dimethano-1H-benz[f]indene (X) had m.p. 155.5-156.5° (from acetone).

Found %: C 44.58, 44.66; H 2.87, 2.90; Cl 52.33, 52.35. $C_{15}H_{12}Cl_6$.

Calculated %: C 44.49; H 2.97; Cl 52.54.

SUMMARY

1. A study was made of the diene condensation of phenyl vinyl, butyl vinyl, and cyclohexyl vinyl ethers with cyclopentadiene.

2. It was shown that this reaction proceeds stepwise and that the second stage can be carried out with other dienes.

3. It was shown that hexachlorocyclopentadiene can be condensed with vinyl ethers and with the adducts formed by vinyl ethers with cyclopentadiene.

4. Ten compounds of the bicyclo[2.2.1]hept-2-ene and octahydro-1,4,5,8-dimethanonaphthalene series containing four and five five-membered rings in their molecules were isolated and characterized. Eight of the compounds prepared have not been described previously in the literature.

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BRIEF COMMUNICATIONS

INVESTIGATION OF THE POROSITY OF NATURAL SORBENTS BY METHODS OF CAPILLARY CONDENSATION AND MERCURY POROMETRY

V. T. Bykov, V. G. Gerasimov, and N. I. Zalevsky

Two ways of determining the structure of porous bodies, namely, capillary condensation of vapor and mercury porometry, have been compared by Soviet investigators in their application to the cases of active carbons [1,2] and aluminum silicate gels [3], and it has been shown that the two methods give agreeing results. It is of considerable interest to make comparative appraisals of the porous structures of natural sorbents by these two methods. The method of vapor sorption, i.e. study of the capillary-condensation process, can give a

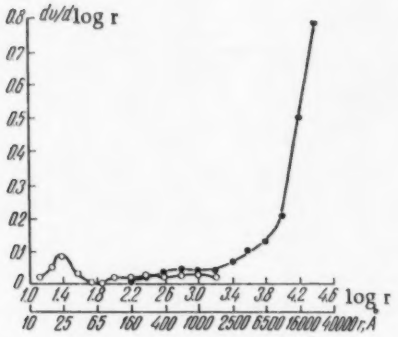

Fig. 1. Differential curve for the pore-volume distribution of suifunite: o - experimental points obtained by capillary condensation; • - experimental points obtained by mercury porometry; Sample No. 55.

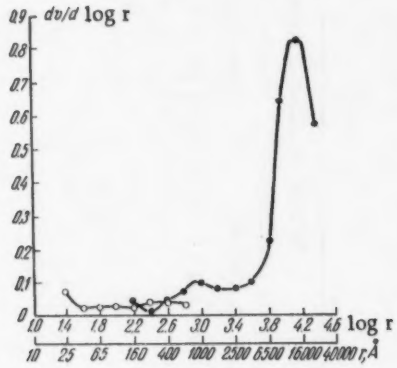

Fig. 2. Differential curve for the pore-volume distribution of tripolite; Sample No. 223.

complete characterization of the distribution of pore volume with respect to effective radius over a wide range of pore size. Mercury porometry, i.e. the forcing in of mercury under pressure, can characterize the pore-volume distribution for pores, ranging from large to transitional in size (as the pressure is increased). Exact or approximate agreement of the results of the two methods in the investigation of the sorbents would serve as mutual confirmation of their soundness.

As previous investigations showed [4], natural sorbents, and in particular sorbents from Far East deposits, are notable for their great variety of porous structures. The transitional pores generally make the greatest contribution to the pore volume (sometimes the macropores make the greatest contribution). The bleaching power of natural sorbents is essentially determined by adsorption at the surface of transitional pores, for, owing to their small specific surface, the macropores play an insignificant part in this process.

TABLE

Comparison of Experimental Data, Obtained by the Two Methods under Comparison, on the Porous Structure of Natural Sorbents

Sample No. 55, Suifunite						Sample No. 223, Tripolite						Sample No. 171					
Capillary-condensation method			Mercury porometry			Capillary-condensation method			Mercury porometry			Capillary-condensation method			Mercury porometry		
r, Å	$\log r$	$\frac{dv}{d\log r}$	r, Å	$\log r$	$\frac{dv}{d\log v}$	r, Å	$\log r$	$\frac{dv}{d\log r}$	r, Å	$\log r$	$\frac{dv}{d\log r}$	r, Å	$\log r$	$\frac{dv}{d\log r} \cdot 10^2$	r, Å	$\log r$	$\frac{dv}{d\log r} \cdot 10^2$
14	1 156	0.025	—	—	—	25	1.4	0.075	—	—	—	10	1.0	1.55	—	—	—
19	1.275	0.050	—	—	—	40	1.6	0.025	—	—	—	16	1.2	0.97	—	—	—
24	1.380	0 090	—	—	—	63	1.8	0.033	—	—	—	25	1.4	1.55	—	—	—
31	1.484	0.033	—	—	—	100	2.0	0.033	—	—	—	40	1.6	2.35	—	—	—
39	1,590	0.004	—	—	—	160	2.2	0.025	160	2.2	0.053	63	1.8	3.10	—	—	—
52	1.714	0.008	—	—	—	250	2.4	0.046	250	2.4	0.016	100	2.0	3 30	—	—	—
72	1.856	0.006	—	—	—	400	2.6	0.043	400	2.6	0,050	160	2 2	2.60	160	2.2	1.98
112	2.050	0.021	—	—	—	840	2.8	0.038	840	2.8	0.075	250	2.4	1.40	250	2.4	1.55
160	2.200	0 015	160	2.2	0 011	1000	3.0	0.038	1000	3.0	0.105	400	2.6	2.10	400	2 6	1.95
250	2.400	0.030	250	2.4	0.031	—	—	—	1590	3.2	0.085	840	2.8	2.65	840	2.8	2.12
400	2.600	0.0275	400	2.6	0 042	—	—	—	2500	3 4	0.085	—	—	—	1000	3.0	3.38
840	2.800	0.030	840	2.8	0.048	—	—	—	4000	3.6	0.100	—	—	—	1590	3.2	4.13
1000	3.000	0.030	1000	3.0	0.041	—	—	—	6500	3.8	0.225	—	—	—	2500	3.4	5.35
1590	3.200	0.020	1590	3.2	0,039	10000	4.0	0.210	10000	4 0	0 640	—	—	—	4000	3.6	1 63
—	—	—	2500	3.4	0.066	16000	4.2	0.814	16000	4.2	0 814	—	—	—	6500	3.8	2.28
—	—	—	4000	3 6	0.103	25000	4.4	0.572	25000	4.4	0.572	—	—	—	10000	4.0	1.66
—	—	—	6500	3.8	0 128												
—	—	—	10000	4.0	0.210												
—	—	—	16000	4.2	0 520												
—	—	—	25000	4.4	0.798												

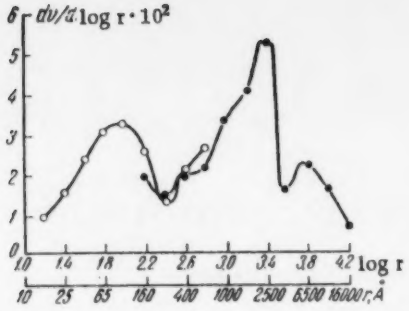

Fig. 3. Differential curve for the pore-volume distribution of Baranov andesite basalt; Sample No. 171

For the experimental part of the study of the structure of natural sorbents we used mercury porometry, but for the study of porosity over a wide range of pore size we determined sorption isotherms for heptane and benzene vapors.

Figures 1-3 give the differential curves for the distribution of pore volume with respect to the logarithm of effective radius. The curves indicated by circles were calculated from the desorption branches of the isotherms, the thickness of the adsorption film being taken into account. The curves indicated by spots were obtained by mercury porometry. The Table gives experimental data obtained by the two methods under comparison. For the decomposed ash rock suifunite (Sample No. 55) and for tripolite (Sample No. 223) the curves agree completely over the range of pore size common to the two methods. For decomposed ash rocks two maxima are present: a small one in the initial part of the curve and a well-marked one in the macropore region. The region of transitional curves is represented by a diffuse curve. In the case of Baranov andesite basalt (Sample No. 171) two maxima are again observed: one in the region of transitional pores, 40-160 A; and the other in the macropore region at 2500 A. In this case there is a slight discrepancy between the curves obtained by the two methods. All three samples of natural sorbents, therefore, have a bidisperse structure.

SUMMARY

1. The porous structures of some natural sorbents (Samples No. 55, 223, and 171) were investigated by the method of sorption and capillary condensation of vapor and by mercury porometry.

2. The results of the investigation indicate that these two methods give agreeing and mutually consistent results.

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BUFFER EFFECT ON SURFACE TENSION IN TERNARY SYSTEMS

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For a ternary system change in surface tension σ can, according to Gibbs, be written as follows:

$$d\sigma = -(\Gamma_0^N d\mu_0 + \Gamma_1^N d\mu_1 + \Gamma_2^N d\mu_2), \tag{1}$$

in which the subscripts 0, 1, 2 correspond to the solvent and the two solutes, Γ_i^N is the adsorption for the case in which concentrations are expressed as mole fractions c_{N_i}, and μ_i is the chemical potential of the component indicated by i. Since

$$\Sigma N_i \cdot d\mu_i = 0 \text{ и } \Sigma\Gamma_i^N = 0, \tag{2}$$

we may eliminate Γ_0^N and $d\mu_0$ from Equation (1):

$$d\sigma = -\frac{1}{1-c_{N1}-c_{N2}}[\Gamma_1^N(1-c_{N2})+c_{N1}\Gamma_2^N]\,d\mu_1 - \\ -\frac{1}{1-c_{N_1}-c_{N_2}}[\Gamma_2^N(1-c_{N_1})+c_{N_2}\Gamma_1^N]\,d\mu_2 \tag{3}$$

In general, the chemical potentials μ_i depend on the activities of all components, and we shall examine this case below. For ideal solutions:

$$d\mu = RTd\ln c_N; \tag{4}$$

and substituting (4) in (3) we obtain:

$$d\sigma = -\frac{RT}{1-c_{N_1}-c_{N_2}}[\Gamma_1^N(1-c_{N_1})+\Gamma_2^N c_{N1}]\,d\ln c_{N1} - \\ -\frac{RT}{1-c_{N_1}-c_{N_2}}[\Gamma_2^N(1-c_{N_1})+\Gamma_1^N c_{N_2}]\,d\ln dC_{N_2} \tag{5}$$

From (5) we may determine the partial derivatives

$$\left(\frac{\partial\sigma}{\partial c_{N_1}}\right)_{c_{N_2}} \text{ и } \left(\frac{\partial\sigma}{\partial c_{N_2}}\right)_{c_{N_1}}$$

$$\left(\frac{\partial\sigma}{\partial c_{N1}}\right)_{c_{N2}} = -\frac{RT}{c_{N_1}(1-c_{N_1}-c_{N_2})}[\Gamma_1^N(1-c_{N2})+\Gamma_2^N c_{N1}]. \tag{6a}$$

$$\left(\frac{\partial\sigma}{\partial c_{N_2}}\right)_{c_{N_1}} = -\frac{RT}{c_{N2}(1-c_{N1}-c_{N2})}[\Gamma_2^N(1-c_{N1})+\Gamma_1^N c_{N2}]. \tag{6b}$$

According to the molecular theory of surface phenomena developed by one of us [1], the adsorption of a given component in a ternary system can be expressed as follows:

$$\Gamma_1^N = -\frac{N}{\omega} c_{N_1} \frac{(e^{\Delta_1} - 1)(1 - c_{N_1}) - (e^{\Delta_2} - 1) c_{N_2}}{1 + (e^{\Delta_1} - 1) c_{N_1} + (e^{\Delta_2} - 1) c_{N_2}}, \tag{7}$$

in which $\Delta_i = \frac{\gamma}{kT}(m_0 - m_i)$, m being the generalized moment of the component concerned, $\gamma > 0$, and k Boltzmann's constant; ω is the surface occupied by N moles.

Substituting (7) and the analogous expression for Γ_2^N in (6a) and (6b), we obtain:

$$\left(\frac{\partial \sigma}{\partial c_{N_1}}\right)_{c_{N_2}} = -\frac{RTN}{\omega} \frac{e^{\Delta_1} - 1}{1 + (e^{\Delta_1} - 1) c_{N_1} + (e^{\Delta_2} - 1) c_{N_2}}. \tag{8a}$$

$$\left(\frac{\partial \sigma}{\partial c_{N_2}}\right)_{c_{N_1}} = -\frac{RTN}{\omega} \frac{e^{\Delta_2} - 1}{1 + (e^{\Delta_1} - 1) c_{N_1} + (e^{\Delta_2} - 1) c_{N_2}}. \tag{8b}$$

If the given ternary system consists of solvent, a surface-active component (subscript 1) and a surface-inactive component (subscript 2), then $\Delta_1 > 0$ and $\Delta_2 < 0$ [1]. For this case it will be seen from Equation (8a) that the curves expressing the relation of surface tension to the concentration of the surface-active component will be steeply sloped.

Since $d\sigma$ is a complete differential, Equation (5) may be integrated after substitution for Γ_1^N and Γ_2^N from Equation (7). Integrating in this way we obtain the following equation for σ in the ternary system:

$$\sigma = \sigma_0 - \frac{RTN}{\omega} \ln [1 + (e^{\Delta_1} - 1) c_{N_1} + (e^{\Delta_2} - 1) C_{N_2}], \tag{9}$$

which in the case of binary systems passes over into the known equation of Shishkovsky:

$$\sigma = \sigma_0 - \frac{RTN}{\omega} \ln [1 + (e^{\Delta_1} - 1) C_{N_1}]. \tag{10}$$

Equation (9) shows that, even in an ideal system, the surface properties of a ternary system are not additive.

Let us now analyze the general case in which chemical potentials depend on the activities of all components of the system:

$$d\mu_1 = RTd \ln f_1 c_{N_1} = RT \left[\frac{\frac{\partial f_1}{\partial c_{N_1}} dc_{N_1} + \frac{\partial f_1}{\partial c_{N_2}} dc_{N_2}}{f_1} + \frac{dc_{N_1}}{c_{N_1}} \right] \tag{11a}$$

$$d\mu_2 = RT\, d \ln f_2 C_{N_2} = RT \left[\frac{\frac{\partial f_2}{\partial c_{N_1}} dc_{N_1} + \frac{\partial f_2}{\partial c_{N_2}} dc_{N_2}}{f_2} + \frac{dc_{N_2}}{c_{N_2}} \right], \tag{11b}$$

(f is activity coefficient).

By the use of (11a) and (11b) we obtain

$$d\sigma = -\frac{RTN}{\omega} \left[\frac{e^{\Delta_1} - 1}{1 + (e^{\Delta_1} - 1) c_{N_1} + (e^{\Delta_2} - 1) c_{N_2}} + \right.$$

$$\left. + \frac{(e^{\Delta_1} - 1) c_{N_1} \cdot \frac{\partial f_1}{\partial c_{N_1}}}{[1 + (e^{\Delta_1} - 1) C_{N_1} + (e^{\Delta_2} - 1) c_{N_2}] f_1} + \right.$$

$$+\frac{(e^{\Delta_2}-1)\,c_{N_2}\dfrac{\partial f_2}{\partial c_{N_1}}}{[1+(e^{\Delta_1}-1)\,c_{N_1}+(e^{\Delta_2}-1)\,c_{N_2}]\,f_2}\Bigg]dc_{N_1}-$$

$$-\frac{RTN}{\omega}\Bigg[\frac{e^{\Delta_2}-1}{1+(e^{\Delta_1}-1)\,c_{N_1}+(e^{\Delta_2}-1)\,c_{N_2}}+$$

$$+\frac{(e^{\Delta_2}-1)\,c_{N_2}\dfrac{\partial f_2}{\partial c_{N_2}}}{[1+(e^{\Delta_1}-1)\,c_{N_1}+(e^{\Delta_2}-1)\,c_{N2}]\,f_2}+$$

$$+\frac{(e^{\Delta_1}-1)\,c_{N_1}\dfrac{\partial f_1}{\partial c_{N_2}}}{[1+(e^{\Delta_1}-1)\,c_{N_1}+(e^{\Delta_2}-1)\,c_{N_2}]\,f_1}\Bigg]dc_{N_2}. \tag{12}$$

From Equation (12) we obtain:

$$\left(\frac{\partial\sigma}{\partial c_{N_1}}\right)_{c_{N_2}}=-\frac{RTN}{\omega}\Bigg[\frac{e^{\Delta_1}-1}{1+(e^{\Delta_1}-1)\,c_{N_1}+(e^{\Delta_2}-1)\,c_{N_2}}+$$

$$+\frac{(e^{\Delta_1}-1)\,c_{N_1}\dfrac{\partial f_1}{\partial c_{N_1}}}{[1+(e^{\Delta_1}-1)\,c_{N_1}+(e^{\Delta_1}-1)\,c_{N_2}]\,f_1}+$$

$$+\frac{(e^{\Delta_2}-1)\,c_{N_2}\dfrac{\partial f_2}{\partial c_{N_1}}}{[1+(e^{\Delta_1}-1)\,c_{N_1}+(e^{\Delta_2}-1)\,c_{N_2}]\,f_2}\Bigg]. \tag{13a}$$

$$\left(\frac{\partial\sigma}{\partial c_{N_2}}\right)_{c_{N_1}}=-\frac{RTN}{\omega}\Bigg[\frac{e^{\Delta_2}-1}{1+(e^{\Delta_1}-1)\,c_{N_1}+(e^{\Delta_2}-1)\,c_{N_2}}+$$

$$+\frac{(e^{\Delta_1}-1)\,c_{N_1}\dfrac{\partial f_1}{\partial c_{N_2}}}{[1+(e^{\Delta_1}-1)\,c_{N_1}+(e^{\Delta_2}-1)\,c_{N_2}]\,f_1}+$$

$$+\frac{(e^{\Delta_2}-1)\,c_{N_2}\dfrac{\partial f_2}{\partial c_{N_2}}}{[1+(e^{\Delta_1}-1)\,c_{N_1}+(e^{\Delta_2}-1)\,c_{N_2}]\,f_2}\Bigg]. \tag{13b}$$

For simplicity in the analysis we shall assume in our further treatment that at low concentrations the activity coefficients are close to unity, but their differential coefficients with respect to concentration are not zero. In our case let the component with subscript 1 be surface-active and the component with subscript 2 be surface-inactive. Let us examine the value of the partial derivative

$$\left(\frac{\partial\sigma}{\partial c_{N_2}}\right)_{c_{N_1}}=-\frac{RTN}{\omega}\left[\frac{(e^{\Delta_1}-1)\,c_{N_1}\dfrac{\partial f_1}{\partial c_{N_2}}+(e^{\Delta_2}-1)+c_{N2}\,(e^{\Delta_2}-1)\dfrac{\partial f_2}{\partial c_{N_2}}}{1+(e^{\Delta_1}-1)\,c_{N_1}+(e^{\Delta_2}-1)\,c_{N_2}}\right]. \tag{14}$$

From investigations of solutions of alcohols in electrolyte solutions it is known that activity coefficients of surface-active substances increase with rise in concentration of the surface-inactive component, i.e. $\frac{\partial f_1}{\partial c_{N_2}}>0$ [2]. As regards metal systems, we have no grounds for supposing that the course of adsorption processes is different in principle[3]. It is known also that for a given component there is always a certain con-

centration range in which the following condition is fulfilled:

$$\left| c_{N_2} \frac{\partial f_2}{\partial c_{N_2}} \right| < 1 . \qquad (15)$$

It follows from Equation (14) that, depending on the concentration of surface-active substance, the surface tension of the system may increase or diminish with increase in the concentration of surface-inactive substance; this has been shown experimentally in various investigations [3,4].

At a certain, so-called buffer, concentration of surface-active substance, $\left(\frac{\partial \sigma}{\partial c_{N_2}}\right)_{c_{N_1}} = 0$. In order to find the value of the buffer concentration we equate the numerator of the expression in Equation 14 to zero and obtain

$$c_{N_1}^{buf} = - \frac{(e^{\Delta_2} - 1)(1 + c_{N_2} \partial f_2 / \partial c_{N_2})}{(e^{\Delta_1} - 1) \partial f_1 / \partial c_{N_2}} . \qquad (16)$$

This equation provides an explanation of the experimentally observed displacement of the buffer concentration toward lower concentrations when the surface-active substance is replaced by a component of still higher surface activity [4]. From Equation (16) it follows also that the buffer concentration of surface-active substance is not independent of the concentration of surface-inactive substance: the curves expressing the relation of the surface tension of the system to the concentration of surface-active substance intersect not in a single point, but over a certain concentration range.

SUMMARY

1. On the assumption that the chemical potentials depend only on the concentrations of the components, an equation is derived for the surface-tension isotherm of a ternary system which, in the case of a binary system, passes into the known Shishkovsky's equation.

2. It is shown that, in a ternary system consisting of solvent, surface-active component, and surface-inactive component, a "quasi-buffer" effect of concentration must occur in a certain concentration range. In the graphical representation of the relation of σ to the concentration of surface-active substance, this effect is manifested by the intersection of the curves within a certain concentration range. The equation obtained provides an explanation of the displacement of the buffer concentration occurring when one component of the system is replaced by another.

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SOME SPECIFIC CHARACTERISTICS OF A SKELETAL NICKEL-ALUMINUM CATALYST IN THE HYDROGENOLYSIS OF A CYCLOPENTANE RING

N. I. Shuikin and M. I. Cherkashin

The catalytic hydrogenolysis of the cyclopentane ring has been studied by many investigators. In a review by Kazansky [1] covering material up to 1948, it is stated that platinized charcoal is a specific catalyst for the hydrogenolysis of C--C bonds of the cyclopentane ring. For comparison purposes, experiments on the hydrogenolysis of cyclopentanes in presence of other catalysts were carried out. Thus, Kazansky and Sergienko [2] investigated the hydrogenolysis of butyl- and isopentyl-cyclopentanes in presence of nickel supported by alumina and found that considerable amounts of degradation products are formed even at 250°.

In the present work our object was to investigate the hydrogenation and hydrogenolysis products from 1-butylcyclopentene, 1-isopentylcyclopentene, and isopentylcyclopentane and to establish the preferred point of rupture in the cyclopentane ring in presence of a nickel-aluminum catalyst.

EXPERIMENTAL

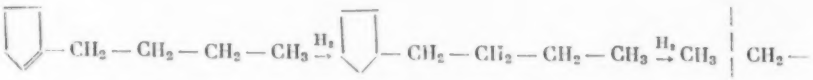
The original hydrocarbons had the following properties: 1-butylcyclopentene, b.p. 156.5° (748 mm), n_D^{20} 1.4488, and d_4^{20} 0.8107; 1-isopentylcyclopentene, b.p. 168-168.5° (760 mm), n_D^{20} 1.4507, and d_4^{20} 0.8151; isopentylcyclopentane, b.p. 171.2° (744 mm), n_D^{20} 1.4337, and d_4^{20} 0.7875.

Their hydrogenolysis was carried out in a flow system over a nickel-aluminum catalyst [3] at 200° and atmospheric pressure. All the hydrocarbons were passed in 50-g portions at a space velocity of 0.06 hour^{-1}. From 1-butylcyclopentene the yield of liquid catalyzate was 66.6%, from 1-isopentylcyclopentene it was 80.1%, and from isopentylcyclopentane it was 82.7%. The catalyzates were fractionated through a column of 40 theoretical plates. On the basis of fractionation curves we isolated narrow fractions consisting of individual substances or mixtures of such substances. The hydrocarbons isolated were examined for their physical constants and were identified from their Raman spectra. The outgoing gases were analyzed chromatographically: they consisted of only hydrogen and methane.

The results are given in Tables 1 and 2.

Table 1 shows that the catalyzate contained about 73% of ring-opening products. In the hydrogenolysis not only 4-methyloctane was formed, but also hydrocarbons having one or two fewer carbon atoms than the original 1-butylcyclopentene. Comparison of the physical constants of the isolated hydrocarbons with reported values [4], and also the Raman spectrum analysis, showed that in this case the hydrogenolysis products were 4-methyloctane, 3-methylheptane, and 2-methylhexane.

Table 2 shows that 1-isopentylcyclopentene yielded 65% of ring-opening products. 2,5-Dimethyloctane and 2,5-dimethylheptane were isolated from the catalyzate. The work revealed for the first time that hydrocarbons containing one or two fewer carbon atoms than the original cyclopentenes are formed. The formation of these products can be explained by the occurrence of secondary hydrogenolysis of 4-methyloctane and 2,5-dimethylheptane as follows:



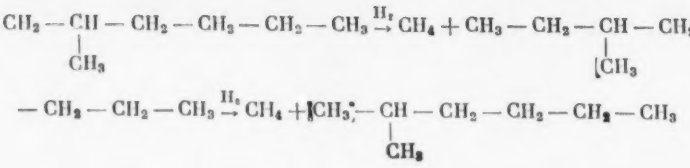


TABLE 1

Products of the Hydrogenolysis of 1-Butylcyclopentene at 200° over a Skeletal Nickel-Aluminum Catalyst

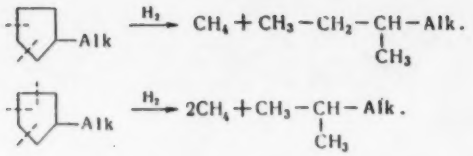
Fraction	B.p. (°C at 760 mm)	n_D^{20}	d_4^{20}	Yield (%)	MR		Hydrogenolysis and hydrogenation products
					Found	Calculated	
I	60.5 - 67.5	1.3746	0.6638	5.9	-	-	
II	67.5 - 89.5	1.3885	0.6683	4.8	-	-	
III	89.5 - 91.5	1.3876	0.6854	4.2	34.45	34.53	2-Methylhexane
IV	91.5 - 118.3	1.3975	0.7042	16.1	-	-	
V	118.3 - 118.5	1.3993	0.7080	12.1	39.04	39.14	3-Methylheptane
VI	118.5 - 140.3	1.4062	0.7200	13.8	-	-	
VII	140.3 - 141.5	1.4064	0.7205	16.6	43.72	43.75	4-Methyloctane
VIII	141.5 - 153.2	1.4162	-	0.9			
IX	153.2 - 155.2	1.4308	0.7848	22.1	-	-	Butylcyclopentane
	Residue			1.1			

TABLE 2

Products of the Hydrogenolysis of 1-Isopentylcyclopentene at 200° over a Nickel-Aluminum Catalyst

Fraction	B.p. (°C at 760 mm)	n_D^{20}	d_4^{20}	Yield (%)	MR		Hydrogenolysis and hydrogenation products
					Found	Calculated	
I	74 - 133	1.3945	0.7000	19.1	-	-	-
II	133 - 135	1.4046	0.7195	9.7	43.67	43.76	2,5-Dimethylheptane
III	135 - 156.4	1.4090	0.7302	8.6	-	-	
IV	156.4 - 157.2	1.4133	0.7377	20.4	48.12	48.38	2,5-Dimethyloctane
V	157.2 - 171	1.4210	0.7585	7.3	-	-	
VI	171 - 172.6	1.4338	0.7884	30.6	-	-	Isopentylcyclopentane
	Residue	—	—	1.2			

It is noteworthy, however, that the structures of these hydrocarbons of lower molecular size indicate absence of hydrogenolysis of the side chain. In all cases the degradation of the cyclopentenes (or isopentylcyclopentane) proceeds by the elimination of a carbon atom which is in the ring and is attached to the C—C bond that is ruptured. We cannot, therefore, exclude the possibility that the opening of the five-membered ring is accompanied by paired ruptures of C—C bonds in the cyclopentane ring:



We may assume that the five-membered ring is disposed on the catalyst surface in such a way that the four CH_2 groups lie in one plane and the fifth, alkyl-substituted group stands out above the surface of the catalyst. This supposition is in accord with the views of Aston [5] and Kilpatrick [6]. In order to determine the effect of the double bond we carried out the hydrogenolysis of isopentylcyclopentane under the same conditions. The catalyzate obtained was extremely similar in character to that obtained from 1-isopentylcyclopentene. This shows that, under our conditions, the cyclopentene is first hydrogenated, and the cyclopentane ring of the product then undergoes hydrogenolysis.

SUMMARY

1. Hydrogenation of 1-butylcyclopentene and 1-isopentylcyclopentene at 200° over a skeletal nickel-aluminum catalyst is accompanied by hydrogenolysis of the cyclopentane ring of the hydrogenation product. Apart from the usual hydrogenolysis products of the cyclopentane, hydrocarbons having one or two fewer carbon atoms than the original hydrocarbon are formed.

2. It was shown that, under the given conditions, isopentylcyclopentane undergoes similar transformations.

3. It was suggested that this behavior of cyclopentanes over a skeletal nickel-aluminum catalyst is to be explained by a special arrangement of the ring on the catalyst surface.

4. An examination is made of two possible variants of the mechanism of the hydrogenolysis of the cyclopentane ring over a skeletal nickel-aluminum catalyst.

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1-PHENYLVINYL COMPOUNDS OF LITHIUM, MERCURY, AND THALLIUM

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In a previous investigation [1] we synthesized various organic compounds of heavy metals. Organometallic compounds in which the metal is attached to olefinic carbon, which we have been investigating in recent years, have still received inadequate study [2]. In the present paper we describe more compounds of this type, namely 1-phenylvinyl compounds of mercury and thallium, which were prepared by the action of mercury and thallium salts on 1-phenylvinyllithium. Some metal derivatives of styrene were studied by Nesmeyanov and Kudryavtseva [3].

1-Phenylvinylmercury bromide, m.p. 89.5-90.5°, which was prepared in 33% yield by the action of mercuric bromide on 1-phenylvinyllithium, is readily symmetrized by gaseous ammonia or sodium stannite with formation of bis-1-phenylvinylmercury (m.p. 68-69°). Reaction of this product with mercuric chloride in acetone gave 1-phenylvinylmercury chloride, m.p. 95.5-96°. In ethereal solution 1-phenylvinyllithium reacts smoothly with thallium tribromide with formation of bis-1-phenylvinylthallium bromide (decomposes at 156-158°). With bis-1-phenylvinylmercury thallium tribromide gives bis-1-phenylvinylthallium bromide in 67% yield, and thallium trichloride gives bis-1-phenylvinylthallium chloride (decomposes at 158-160°) in 70% yield. Like diisopropenylthallium bromide, bis-1-phenylvinylthallium bromide reacts with mercury in acetone with formation of bis-1-phenylvinylmercury in 66% yield.

Unlike isopropenyltin compounds [1], 1-phenylvinyltin compounds could not be obtained by reaction between bis-1-phenylvinylmercury and a stannous halide in acetone, benzene, or petroleum ether solution; neither could they be obtained by reaction between bis-1-phenylvinylthallium bromide and stannous bromide or chloride.

EXPERIMENTAL

Ethereal Solution of 1-Phenylvinyllithium. This was prepared in a three-necked flask in an atmosphere of nitrogen from 0.76 g (0.054 mole) of lithium in 140 ml of dry ether and 10 g (0.054 mole) of α-bromostyrene (b.p. 66° [6 mm], n_D^{25} 1.5870) in 25 ml of ether. The bromostyrene was added at 8-10° over a period of 90 minutes.

1-Phenylvinylmercury Bromide. Over a period of 30 minutes at 8-10°, 16 g (0.044 mole) of mercuric bromide was added slowly to the ethereal solution of 1-phenylvinyllithium obtained, as described above. The reaction mixture was warmed. After being stirred for one hour, the mixture was decomposed with 1% hydrobromic acid. The ethereal solution was washed with water and dried. Ether was evaporated at the water pump, and the residue was repeatedly recrystallized from acetone. The product, amounting to 7 g (33%), consisted of needles, m.p. 89.5-90.5°.

Found %: C 24.92, 24.93; H 1.89, 1.90. C_8H_7HgBr.

Calculated %: C 25.04; H 1.84.

1-Phenylvinylmercury bromide is readily soluble hot in acetone, chloroform, and benzene, less readily soluble in methanol and ethanol, and sparingly soluble in petroleum ether and carbon tetrachloride.

Symmetrization of 1-Phenylvinylmercury Bromide. A. A solution of 7.9 g (0.02 mole) of 1-phenylvinylmercury bromide in 65 ml of benzene was treated with dry ammonia for 90 minutes. The residue was filtered off, and benzene was evaporated from the filtrate at the water pump. Recrystallization of the residue

from 3 : 1 methanol-acetone gave 3.4 g (82%) of crystals, m.p. 68-69°. Further recrystallization did not affect the melting point.

Found %: C 47.47, 46.89; H 3.52, 3.36. $C_{16}H_{14}Hg$.

Calculated %: C 47.23; H 3.47.

Bis-1-phenylvinylmercury is soluble in benzene, acetone, and petroleum ether; it is sparingly soluble in methanol and ethanol.

B. Water (10 ml) and alkaline sodium stannate prepared from 0.65 g (0.0028 mole) of $SnCl_2 \cdot 2H_2O$, 0.5 g of NaOH, and 12 ml of water were added to a solution of 2 g (0.0052 mole) of 1-phenylvinylmercury bromide in 5 ml of acetone. After one hour the precipitate was filtered off, washed with water, dried, and crystallized from petroleum ether. The crystalline product, which amounted to 0.89 g (84%), had a melting point, and also a mixture melting point, of 68.5-69°.

1-Phenylvinylmercury Chloride. Reaction between 1 g (0.0024 mole) of bis-1-phenylvinylmercury in 2 ml of acetone and 0.66 g (0.0024 mole) of mercuric chloride gave 1.44 g (86%) of leaflets, m.p. 95-96°.

Found %: C 28.22, 28.23; H 2.16, 2.03. C_8H_7HgCl.

Calculated %: C 28.33; H 2.08.

1-Phenylvinylmercury chloride is readily soluble hot in acetone, methanol, and ethanol; it is sparingly soluble in petroleum ether.

Bis-1-phenylvinylthallium Bromide. A. A solution of 8 g (0.018 mole) of thallium tribromide in 35 ml of ether was added to the ethereal solution of 1-phenylvinyllithium. The mixture was stirred for 30 minutes and then decomposed with 1% hydrobromic acid. After being washed and dried, the precipitate weighed 4.94 g. Recrystallization from acetone gave 3.01 g (22%) of needles, which decomposed without melting at 156-158°. This substance is soluble in pyridine, sparingly soluble in acetone, very sparingly soluble in methanol and ethanol, and insoluble in petroleum ether.

Found %: C 39.23, 39.29; H 3.01, 3.00; Br 16.25, 16.39. $C_{16}H_{14}TlBr$.

Calculated %: C 39.17; H 2.88; Br 16.29.

B. A solution of 0.82 g (0.0018 mole) of thallium tribromide in 3.5 ml of ether was added to 1.5 g (0.0037 mole) of bis-1-phenylvinylmercury in 3 ml of ether. After one hour the precipitate was filtered off and washed repeatedly with cold acetone. Recrystallization from acetone gave 0.61 g (67%) of bis-1-phenylvinylthallium bromide, which decomposed at 156-158°.

Found %: C 39.31, 39.30; H 2.95, 2.98; Br 16.45, 16.48. $C_{16}H_{14}TlBr$.

Calculated %: C 39.17; H 2.88; Br 16.29.

Some of the solvent was evaporated from the main filtrate, and 1.11 g (78%) of 1-phenylvinylmercury bromide was isolated; its melting point, and also its mixture melting points, was 89-90.5°.

Bis-1-phenylvinylthallium Chloride. Reaction between 1.5 g (0.0037 mole) of bis-1-phenylvinylmercury and 0.55 g (0.0017 mole) of thallium trichloride under conditions similar to those of the reaction with thallium tribromide gave 0.58 g (70%) of fine needles which decomposed at 158-160°.

Found %: C 42.85, 43.10; H 3.21, 3.16; Cl 7.75, 8.03. $C_{16}H_{14}TlCl$.

Calculated %: C 43.07; H 3.16; Cl 7.95

Bis-1-phenylvinylthallium chloride is readily soluble in pyridine, sparingly soluble in acetone, methanol, and ethanol, and insoluble in petroleum ether. The filtrate yielded 0.95 g (76% of 1-phenylvinylmercury chloride, m.p. 95-96°.

Reaction between Bis-1-phenylvinylthallium Bromide and Mercury. A mixture of 1.0 g (0.002 mole) of bis-1-phenylvinylthallium bromide, 10 g of mercury, and 25 ml of acetone was stirred for five hours at 40°. The clear solution was decanted, solvent was evaporated, and the residue was recrystallized from 1 : 3 methan-

ol-acetone. The product amounting to 0.55 g (66%), was bis-1-phenylvinylmercury, m.p. 68-69°. The melting point was not affected by admixture of known bis-1-phenylvinylmercury.

SUMMARY

Methods are described for the preparation of 1-phenylvinyl compounds of mercury and thallium from the salts of these metals and 1-phenylvinyllithium. Some chemical properties of these compounds were investigated.

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MECHANISM OF THE AZOXY-COUPLING REACTION*

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The mechanism of the condensation of nitroso compounds with arylhydroxylamines (the so-called azoxy-coupling reaction) has been frequently discussed in the literature, and most authors [1-4] consider that the process probably proceeds through the stage of the formation of intermediate compounds of the type (I) (see, however, [5]):

$$RNO + R'NHOH \rightarrow \underset{\underset{HO}{|}}{RN} - \underset{\underset{OH}{|}}{NR'} \xrightarrow{-H_2O} \underset{\underset{O}{\downarrow}}{RN} = NR' + RN = \underset{\underset{O}{\downarrow}}{NR'}$$

(I)

However, the mechanism of azoxy coupling has never been studied experimentally, and the available data on the conditions of formation and the properties of azoxy compounds give no definite indications of the character of the intermediate stages of the reaction, so that all statements concerning these matters that have appeared in the literature remain purely hypothetical.

We considered that with the aid of labeled atoms we might make an approach to the solution of the question of the mechanism of azoxy coupling by determining whether the process really does pass through the stage of the formation of intermediate compounds of type (I). When R = R', these compounds, unlike the initial and final substances, contain chemically equivalent nitrogen atoms. Hence, if we synthesize a simple azoxy compound, such as azoxybenzene, but first label one of the reactants, e.g. nitrosobenzene, with N^{15}, it is possible to get an idea of the identity of the intermediate compound from the distribution of the excess of N^{15} between the two nitrogen atoms of the azoxybenzene formed. In fact, if the excess of N^{15} contained in the nitrosobenzene taken was found to be distributed equally between the two nitrogen atoms of the azoxybenzene obtained, this would be a direct indication of the formation of a symmetrical compound as intermediate product, e.g. (II) or some analogous substance:

$$C_6H_5N^{15}O + C_6H_5N^{14}HOH \rightarrow \underset{\underset{HO}{|}}{C_6H_5N^{15}} - \underset{\underset{OH}{|}}{N^{14}C_6H_5} \xrightarrow{-H_2O}$$

(II)

$$\rightarrow \left[\tfrac{1}{2}\, \underset{\underset{O}{\downarrow}}{C_6H_5N^{15}} = N^{14}C_6H_5 + \tfrac{1}{2}\, C_6H_5N^{15} = \underset{\underset{O}{\downarrow}}{N^{14}C_6H_5} \right]$$

*Communication 8 of the Series "Compounds Labeled with C^{14} and N^{15}."

In the experimental study of this problem it is necessary to take account of the readiness with which the reactants undergo change, for it is known (see, e.g., [6,7]) that under the usual azoxy-coupling conditions phenylhydroxylamine may be partially oxidized to nitrosobenzene, which may itself be converted into phenylhydroxylamine. Such side reactions may greatly distort the true picture of the distribution of the excess of N^{15} between the nitrogen atoms of azoxybenzene. It was therefore necessary to find conditions of azoxy coupling under which the side reactions are eliminated or greatly suppressed.

It was shown that in reaction in an alkaline medium* in absence of oxygen at room temperature for two minutes neither phenylhydroxylamine nor nitrosobenzene, taken separately, are converted into azoxybenzene, whereas, when present together, they give azoxybenzene in a yield of more than 90%. We used these conditions in the synthesis of labeled azoxybenzene from $C_6H_5N^{15}O$ and $C_6H_5N^{14}HOH$. In order to study the isotopic compositions of the nitrogen atoms of the azoxybenzene obtained, this was subjected to the following reactions:

$$C_6H_5\overset{\downarrow}{\underset{O}{N}}=NC_6H_5 \xrightarrow{Br_2} C_6H_5\overset{\downarrow}{\underset{O}{N}}=NC_6H_4Br\text{-}p \xrightarrow{Sn+HCl} C_6H_5NH_2 + H_2NC_6H_4Br\text{-}p$$

Aniline and p-bromoaniline were separated in the form of the acetyl derivatives, which were converted into ammonia by the Kjeldahl method; the resulting samples of ammonia were oxidized with sodium hypobromite to nitrogen, the isotopic composition of which was then determined with the mass spectrometer. The results are given in the Table.

TABLE

Substance	N^{15} content (atoms %) Found	Calculated
Nitrosobenzene	37.2	
Acetanilide	19.1	(37.2+0.38):2 =
p-Bromoacetanilide	18.2	= 18.8

The results show that the excess of N^{15} contained in the original nitrosobenzene was distributed equally (accurately within 3%) between the two nitrogen atoms of the azoxybenzene. It follows that its formation is preceded by the formation of an intermediary containing two chemically equivalent nitrogen atoms.

It should be noted that, since the two nitrogen atoms of labeled azoxybenzene synthesized by azoxy coupling have the same isotopic composition, such azoxybenzene cannot be used for the determination of the mechanisms of various isomerizations of azoxy compounds (the Wallach rearrangement and related reactions). For the study of these problems it is necessary to have azoxybenzene in which only one of the nitrogen atoms is labeled with N^{15}, e.g. $C_6H_5\overset{\downarrow}{\underset{O}{N^{14}}}=N^{15}C_6H_5$. We prepared such azoxybenzene from $C_6H_5N^{15}H_2$ and unlabeled o-nitrobenzaldehyde (cf. recently described syntheses of substituted azoxybenzenes [9]) and used it for the study of the mechanism of the above-mentioned isomerizations of azoxy compounds. The results of these investigations will be given in a separate communication.

EXPERIMENTAL

Azoxy Coupling. All operations, including the dissolution of the reactants, were carried out in an atmosphere of nitrogen. A solution of 0.5 g of nitrosobenzene-N^{15}** in 10 ml of alcohol was cooled to 10-12° and added to a stirred solution, also cooled to 10-12°, of 0.5 g of unlabeled phenylhydroxylamine (m.p. 81°) in 10 ml of alcohol; the temperature of the mixture then rose to 16-18°. The resulting green solution was

*It is known [3,8] that the presence of alkali greatly accelerates azoxy coupling, while having little effect on side reactions.

**Nitrosobenzene-N^{15}, m.p. 68° (from alcohol), was obtained in 60% yield by persulfate oxidation, under the usual conditions, of aniline-N^{15}, the synthesis of which has been described previously [10].

stirred rapidly while 0.8 ml of 7% alcoholic KOH was added dropwise (the temperature rose to 20-22°). After a period of two minutes (reckoned from the time when the first drop of alkali was added) the dark-red solution was neutralized with 2 N H_2SO_4; 100 ml of 2% H_2SO_4 was then added. Azoxybenzene separated as an oil, which gradually solidified in the course of 12-15 hours at 0°; weight 0.86 g (92%). The product was dissolved in benzene and treated chromatographically with alumina (elution eith benzene). The yield of azoxybenzene--N^{15}, m.p. 36°, was 0.79 g (85%).

Preparation of 4-Bromoazoxybenzene-N^{15}. This was prepared by the bromination of 1.5 g of azoxybenzene-N^{15} under previously described conditions [11]; yield 1.7 g (81%); m.p. 73° (from alcohol).

Scission of 4-Bromoazoxybenzene-N^{15}. A mixture of 1.5 g of bromoazoxybenzene-N^{15}, 1.5 g of tin (fine turnings), and 10 ml of concentrated hydrochloric acid was heated at 70-80° with frequent shaking until the tin had dissolved. Heating was continued with addition of two further portions (0.75 g) of tin and two further portions (5 ml) of acid until a clear solution had been formed. This solution was made alkaline and aniline and p-bromoaniline were steam-distilled off. The acidified distillate (about 200 ml) was evaporated down to 8-10 ml, and then made alkaline and extracted several times with ether. The ether extract was dried, ether was distilled off, and 1.5 ml of water and 0.5 ml of acetic anhydride was added to the residue. The mixture was shaken until a solid mass had formed. Water (50 ml) was added, and the precipitate of p--bromoacetanilide was filtered off and washed with 30-50 ml of water. The filtrate and washings, which contained acetanilide, were evaporated to dryness. The amounts isolated were 1.05 g (90%) of p-bromoacetanilide, m.p. 166-167° (from water) and 0.28 g (38%) of acetanilide, m.p. 113-114° (from water in presence of charcoal). The determination of the isotopic composition of the nitrogen atoms of the anilides is described above.

SUMMARY

1. The mechanism of azoxy coupling was studied, the example taken being the formation of azoxybenzene from $C_6H_5N^{15}O$ and $C_6H_5N^{14}HOH$.

2. It was shown that the formation of the azoxy compound from the arylhydroxylamine and the nitroso compound is preceded by the formation of an intermediary of type (II), in which the nitrogen atoms are chemically equivalent.

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NEW METHOD OF SYNTHESIZING MACROCYCLIC COMPOUNDS

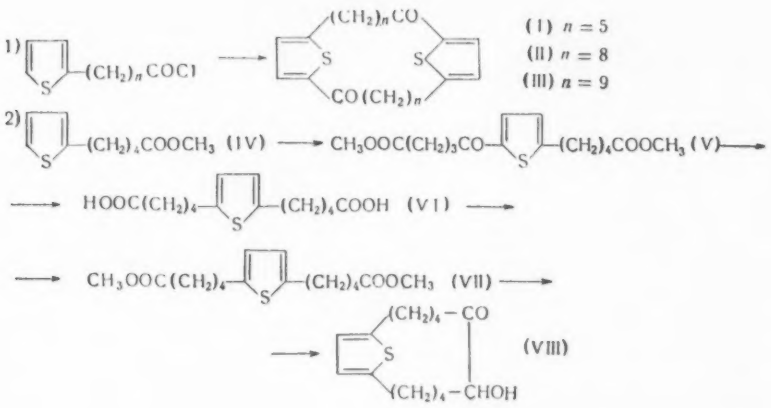
PREPARATION OF ALICYCLIC COMPOUNDS FROM THIOPHENE DERIVATIVES

Ya. L. Goldfarb, S. Z. Taits, and L. I. Belenky

The methods now known for the synthesis of macrocyclic compounds give yields that are acceptable for practical purposes. The scope of the methods is still rather restricted, however, and there are often fundamental difficulties to overcome in the preparation of the bifunctional compounds required for cyclization.

Reductive desulfurization of thiophene derivatives in presence of Raney nickel, which has received extensive application in our laboratory in recent years, enables us to prepare aliphatic compounds of various types. We can envisage two ways in which this principle can be applied in the synthesis of macrocyclic compounds: 1) the preparation of long-chain bifunctional aliphatic compounds (e.g. dicarboxylic and hydroxy acids [1,2]) capable of being cyclized into macrocycles by known methods; and 2) the synthesis of bi- or poly-cyclic compounds containing thiophene rings and subsequent elimination of the sulfur bridges with the aid of nickel. The second way, which is based on the conversion of polycyclic compounds into monocycles and which offers, at the same time, the possibility of making use of the aromatic character of the thiophene ring not only for the introduction of various substituents, but also for the effecting of cyclization, is new in principle.

As far as we know, until recently only one macrocyclic compound containing thiophene rings had been described [3], but its structure has not been proved. We synthesized compounds of this type, i.e. containing thiophene rings, in the following ways:



Both reactions were carried out at high dilution. Cyclization by internal acylation (Scheme 1) was carried out either in boiling ethereal aluminum chloride or at +5° with the aid of stannic chloride in benzene. The acyloin condensation (Scheme 2) was carried out in presence of finely divided sodium in ether-xylene solution at 60°. It should be noted that, in the cyclization stage, we have as yet succeeded in obtaining yields of only 15% (Scheme 1) and 25-30% (Scheme 2). We began with the investigation of internal acylation and expected to obtain compounds containing one thiophene ring, but, in spite of high dilution, we succeeded in

isolating only products of the intermolecular cyclization of two molecules of acid chloride. Nevertheless, we consider that by the use of other reactants (e.g. substances derived from dithienylalkanes) it may be possible to obtain "monomeric" macrocyclic systems which are the products of intramolecular acylation in the narrow sense of this word. A macrocyclic system containing one thiophene ring was obtained by the acyloin condensation of the diester (VII).

Four of the five macrocyclic compounds containing thiophene rings which we prepared were subjected to reductive desulfurization, and high yields of the corresponding alicyclic compounds were obtained. It should be noted that the reductive desulfurization of diketones was carried out in presence of acetone; this appeared to make it possible to obtain pure alicyclic diketones without admixture of their reduction products.

EXPERIMENTAL

1. The diketone (I), prepared by the cyclization of 2-thiophenehexanoyl chloride [4], has m.p. 142--143.5°.

Found %: C 66.60, 66.63; H 6.68, 6.64; S 17.75, 17.64. $C_{20}H_{24}O_2S_2$.

Calculated %: C 66.60; H 6.74; S 17.78.

Found M: 350 (Rast's method)

Calculated M: 360.54

2. The diketone (II), prepared by the cyclization of 2-thiophenenonanoyl chloride [5], has m.p. 83.5--85°.

Found %: C 70.03, 69.96; H 8.29, 8.15; S 14.61, 14.46. $C_{26}H_{36}O_2S_2$.

Calculated %: C 70.22; H 8.16; S 14.42.

Found M: 432 (cryoscopically in benzene).

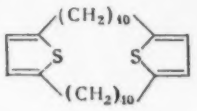
Calculated M: 444.68.

3. The diketone (III), prepared by the cyclization of 2-thiophenedecanoyl chloride [4], has m.p. 99.5-101°.

Found %: C 70.84, 70.96; H 8.61, 8.55; S 13.37, 13.12. $C_{28}H_{40}O_2S_2$.

Calculated %: C 71.13; H 8.53; S 13.57.

Kizhner reduction of this diketone gave the tricyclic compound (IX)



(IX)

which melts at 51.5-53.5°.

Found %: C 75.54, 76.04; H 9.88, 9.98; S 14.64, 14.68. $C_{28}H_{44}S_2$.

Calculated %: C 75.60; H 9.97; S 14.42.

Found M: 446 (cryoscopically in benzene).

Calculated M: 444.70.

4. The acyloin (VIII), prepared by the cyclization of the diester (VII), has m.p. 69.5-71°.

Found %: C 66.77, 66.47; H 7.98, 8.04; S 12.53, 12.26. $C_{14}H_{20}O_2S$.

Calculated %: C 66.60; H 7.97; S 12.71.

Found M: 266 (cryoscopically in benzene).

Calculated M: 253.37.

The diester (VII) was prepared from 2-thiophenevaleric acid [6] in an overall yield of 54%. The previously undescribed intermediate products had the following constants: methyl 2-thiophenevalerate (IV), b.p. 141.5-143° (14 mm), n_D^{20} 1.5067, d_4^{20} 1.0894, found MR 54.13, calculated MR 53.93; dimethyl δ-oxo-2,5--thiophenedivalerate (V), m.p. 67.5-69°.

Found %: C 58.72; H 6.81; S 10.01. $C_{16}H_{22}O_5S$.

Calculated %: C 58.87; H 6.79; S 9.82.

2,5-thiophenedivaleric acid (VI) has m.p. 140.5-142.5°; and its dimethyl ester (VII) has b.p. 182-185° (1 mm), n_D^{20} 1.5000, d_4^{20} 1.0968, found MR 83.93, calculated MR 84.18.

Found %: C 61.75; H 7.67. $C_{16}H_{24}O_4S$.

Calculated %: C 61.53; H 7.71.

5. Reductive desulfurization of the diketone (I) gave 1,11-cycloeicosanedione, m.p. 50.5-52°.

Found %: C 77.56, 77.60; H 11.51, 11.67. $C_{20}H_{36}O_2$.

Calculated %: C 77.85; H 11.76.

The literature gives m.p. 48-51° [7] and 49-51° [8].

6. Reductive desulfurization of the diketone (II) gave 1,14-cyclohexacosanedione, m.p. 69-70°.

Found %: C 79.33, 79.33; H 12.34, 12.37. $C_{26}H_{48}O_2$.

Calculated %: C 79.53; H 12.32.

The literature [9] gives m.p. 68-69°.

7. Reductive desulfurization of the diketone (III) gave 1,15-cyclooctacosanedione, m.p. 71.5-72.5°.

Found %: C 79.81, 79.53; H 12.47, 12.30. $C_{28}H_{52}O_2$.

Calculated %: C 79.93; H 12.46.

The literature [9] gives m.p. 72-73°.

Reductive desulfurization of (IX) [the reduction product of the diketone (III)] gave cyclooctacosane, m.p. 49-49.5°.

Found %: C 85.58, 85.87; H 14.30, 14.31. $C_{28}H_{56}$.

Calculated %: C 85.63; H 14.37.

The literature [9] gives m.p. 47-48°.

SUMMARY

1. Some macrocyclic compounds containing thiophene rings were prepared.

2. A new method was proposed for the preparation of large-ring alicyclic compounds. It includes reductive desulfurization of the corresponding macrocycles containing thiophene rings.

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NEW METHOD OF SYNTHESIZING DIETHYLAMINOMETHYL DERIVATIVES OF SUBSTITUTED PROPARGYL ALCOHOLS

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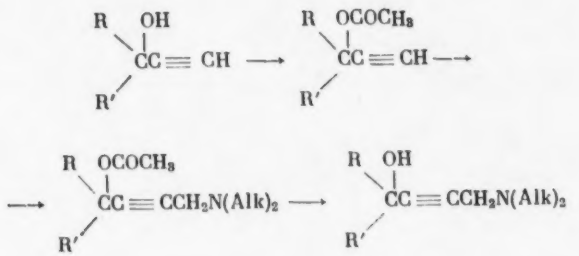
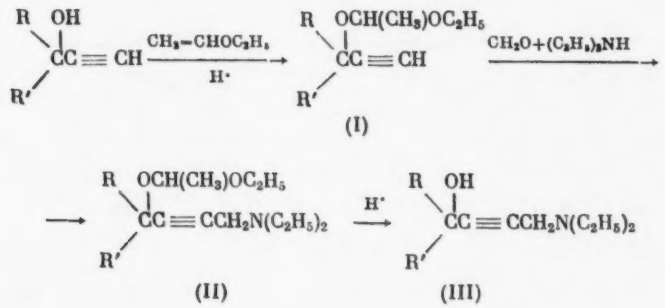
It is known [1] that substituted propargyl alcohols RR'C(OH)C≡CH undergo the Mannich reaction with great difficulty and give very low yields of the corresponding dialkylaminomethyl derivatives. For this reason the conversion of acetylenic alcohols RR'C(OH)C≡CH into amino alcohols RR'C(OH)C≡CCH$_2$N(Alk)$_2$ has been carried out by a roundabout way [1,2]:



However, this method does not enable us to prepare amino alcohols in which R and R' are aromatic radicals, because the corresponding acetylenic alcohols are very labile both in acid and in alkaline media.

We investigated a method by which acetylenic amino alcohols can be obtained under very mild conditions:



(I)

(II) (III)

The acetals (I) were synthesized by the method described by Shostakovsky and Shikhiev [3]. Reaction of the acetals (I) with paraform and diethylamine proceeds smoothly, but slowly; in order to obtain high yields of the amino acetals (II) the mixture must be heated for many hours in dioxane solution. The amino acetals were hydrolyzed by treatment with 5% sulfuric acid, and the amino alcohols (III) were then obtained in high yields.

EXPERIMENTAL

Reaction of Acetylenic Alcohols with Ethyl Vinyl Ether. A Mixture of 1 mole of the acetylenic alcohol and 1.3-1.4 moles of ethyl vinyl ether was prepared in a three-necked flask fitted with reflux condenser, thermometer, and dropping funnel. Addition was made of 2 ml of dry ether containing dry hydrogen chloride, and the mixture was shaken. After a few minutes a vigorous reaction set in, and external cooling was applied to maintain the temperature in the flask at about 50°. When exothermic reaction ceased, the contents of the flask were heated for one hour at 50-60° and then set aside overnight. On the next day the reaction mixture was shaken with 10% aqueous potassium carbonate solution. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and ether extract were combined, dried with magnesium sulfate, and fractionated. The properties of the acetals (I) obtained in this way are given in Table 1.

TABLE 1

R	R′	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR Found	MR Calc.	Yield (%)	Found % C	Found % H	Calc. % C	Calc. % H
CH_3	CH_3*	60—62 (36)	1.4169	—	—	—	94	—	—	—	—
CH_3	C_2H_5	40—43 (8)	1.4204	0.8696	49.51	49.60	64	70.29 70.34	10.61 10.51	70.58	10.58
CH_3	C_6H_5	79—81 (1)	1.4941	0.9820	64.63	64.47	78	76.90 76.90	8.39 8.29	77.06	8.25
$(CH_2)_5$		115—116 (25)	1.4547	0.9398	56.55	56.64	86	73.44 73.27	10.27 10.18	73.48	10.20

*[3].

Reaction of Acetals with CH_2O and $(C_2H_5)_2NH$. A mixture of 1 mole of the acetal, 1.1-1.2 moles of paraform, 1.1 moles of diethylamine, and 80-100 ml of dioxane was prepared in a round-bottomed flask fitted with reflux condenser. The mixture was boiled for 50-60 hours, the water that separated was removed, 50-75 ml of dioxane was added, and the mixture was boiled further for 30-55 hours. The reaction mixture was shaken three times with water in a separating funnel. The organic layer was separated, and the aqueous layer was extracted with ether. The ether extract and organic layer were combined, dried with magnesium sulfate, and fractionated. The properties of the amino acetals (II) obtained in this way are given in Table 2.

TABLE 2

R	R′	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR Found	MR Calc.	Yield (%)	Found N, %	Calc. N, %
CH_3	CH_3	76—79 (2)	1.4414	0.8888	71.66	72.01	81	6.19 6.23	5.81
CH_3	C_2H_5	90—93 (2)	1.4472	0.8910	76.54	76.63	75	5.41 5.51	5.49
CH_3	C_6H_5	134—136 (2)	1.4940	0.9578	92.09	91.50	77	4.75 4.83	4.62
$(CH_2)_5$		118—120 (3)	1.4671	0.9298	83.64	83.67	97	4.96 5.04	4.98

*On the amount of acetal that reacted.

Hydrolysis of Amino Acetals. A mixture of 200 ml of 5% aqueous sulfuric acid and 0.05 mole of the amino acetal was prepared in a three-necked flask fitted with mechanical stirrer, dropping funnel, and condenser set for distillation. The reaction mixture was stirred at room temperature for 6-9 hours, cooled with ice, neutralized with potassium carbonate, saturated with solid sodium hydroxide, and repeatedly extracted with ether. The ether extract was dried with potassium carbonate and fractionated. The properties of the amino alcohols (III) obtained in this way are given in Table 3.

TABLE 3

R	R′	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR Found	MR Calc.	Yield (%)	Found N, %	Calc. N, %
CH_3	CH_3*	72—73 (2)	1.4634	—	—	—	98	—	—
CH_3	C_2H_5	79—80 (2)	1.4661	0.9027	56.15	56.40	92	7.89 8.05	7.65
CH_3	C_6H_5	129—131 (1)	1.5282	**	—	—	94	5.78 5.82	6.06
$(CH_2)_5$***		114—115 (2)	1.4947	0 9608	63.40	63.43	94	6.91 7.08	6.70

*[2]. ** Very viscous oil. *** [4].

SUMMARY

A new method of preparing acetylenic alcohols (III) is proposed.

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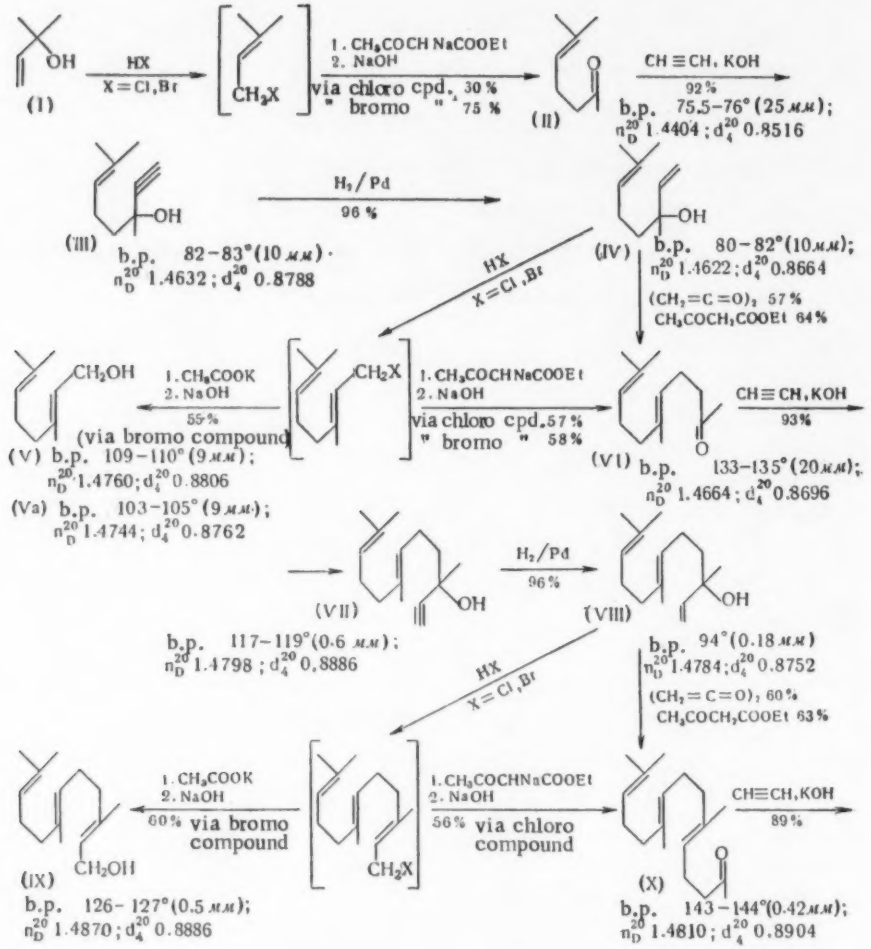
*In Russian.

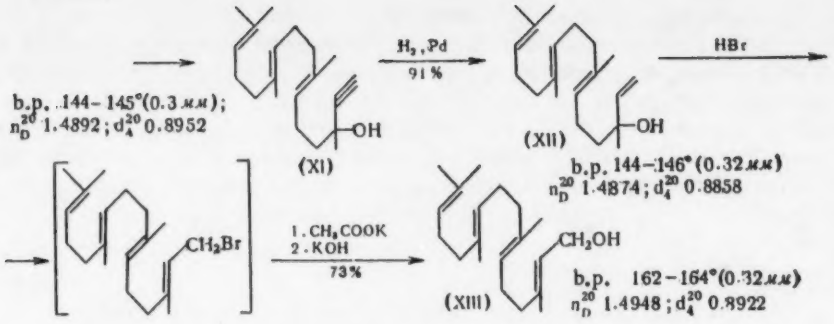
TOTAL SYNTHESIS OF ISOPRENOID ALCOHOLS

I. N. Nazarov, B. P. Gusev, and V. I. Gunar

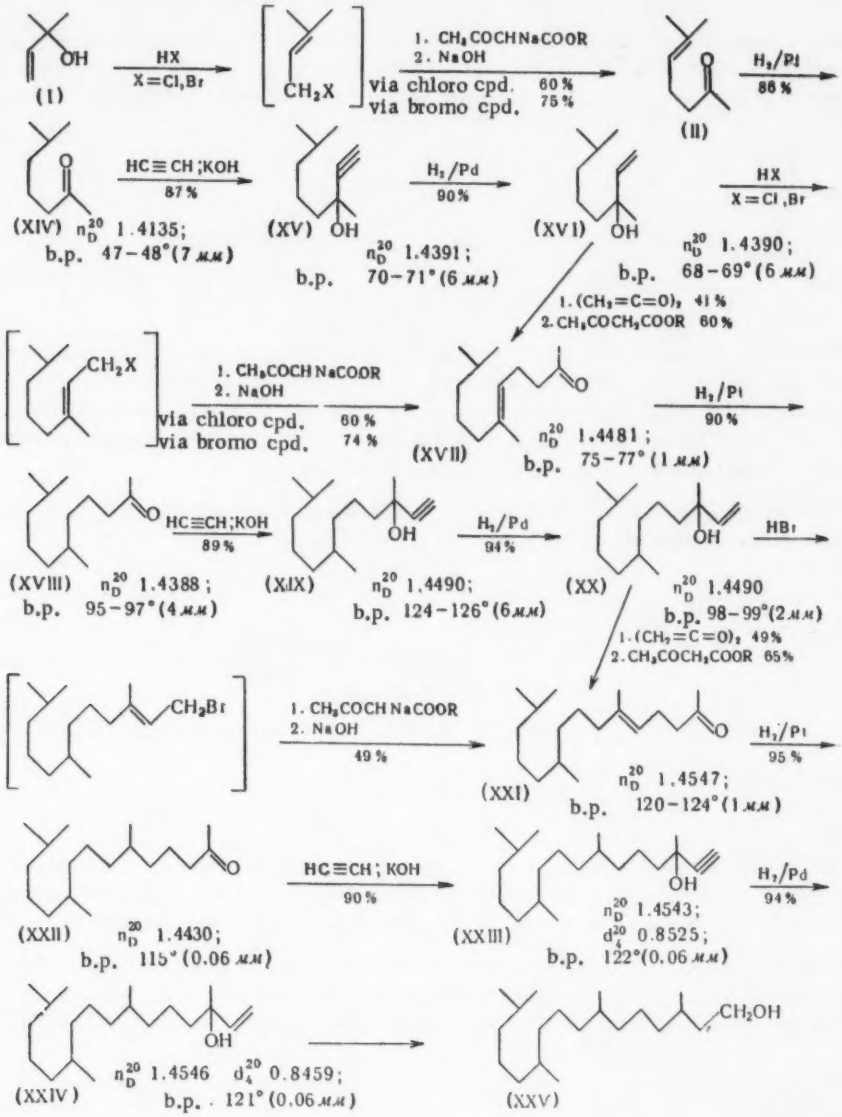
We have made a detailed investigation of the preparation of isoprenoid alcohols (linalool, geraniol, nerol, nerolidol, farnesol, geranyllinalool, geranylgeraniol, and phytol) by the use of the succession of reactions: condensation of ketones with acetylene, selective hydrogenation of acetylenic alcohols, isomerization of tertiary ethylenic alcohols into the corresponding primary alcohols of the allyl type, and the conversion of these into unsaturated ketones of the allylacetone type (acetonation). The whole course of this synthesis and the results obtained are represented in the following schemes:

Synthesis of Linalool (IV), Geraniol (V), Farnesol (IX), Geranylgeraniol (XIII), and Intermediate Compounds:

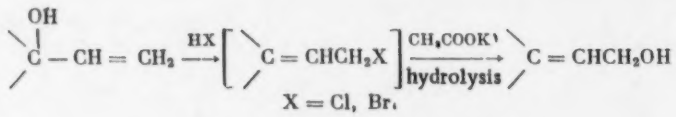




Synthesis of Phytol (XXV) and Intermediate Compounds:

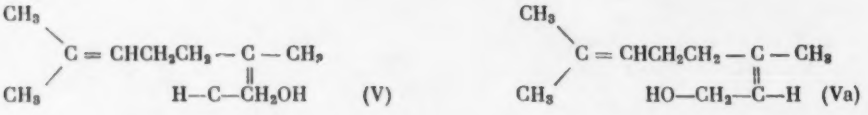


The per cent yields are given below the arrows, and the constants of the products (b.p., n_D^{20}, d_4^{20}) below the formulas. All condensations of ketones with acetylene were carried out by the method developed in our laboratory [1] at 0-20° in presence of potassium hydroxide powder under a pressure of acetylene of 5-8 atm. Until now such condensations were carried out in liquid ammonia and the yields of acetylenic alcohols were lower [2]. The selective hydrogenation of the acetylenic alcohols was always carried out in presence of palladium supported by calcium carbonate [3]. The tertiary ethylenic alcohols obtained in this way were converted into primary alcohols of the allyl type by the action of gaseous hydrogen chloride or bromide with subsequent treatment of the primary halo compounds with a solution of potassium acetate in dimethylformamide and hydrolysis:



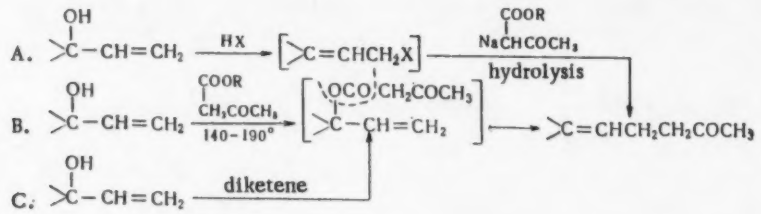
These reactions were carried out in one stage without isolation of intermediate products.

In the isomerization of linalool (IV) in this way, a mixture of geraniol (V) and nerol (Va) was formed in an overall yield of about 55%. The proportions depend greatly on the experimental conditions. At high temperatures (60-70°) the main product is nerol, but at lower temperatures (20-60°) geraniol predominates in the mixture:



Geraniol and nerol can be readily and almost completely separated by chromatography on alumina: nerol is completely eluted with petroleum ether, after which geraniol is eluted with methanol. In the similar isomerization of nerolidol (VIII) and geranyllinalool (XII), farnesol (IX) and geranylgeraniol (XIII) are obtained in yields of about 65% and 75%, respectively. In a similar way we synthesized also isophytol (XXIV), phytol (XXV), and all the intermediate products associated with this synthesis.

The conversion of tertiary ethylenic alcohols into unsaturated ketones of the allylacetone type was effected in three different ways, which are illustrated in the following schemes:



All these reactions were carried out in one stage without isolation of intermediate products. The best method for large amounts is the direct reaction of the tertiary ethylenic alcohols with acetoacetic ester at 140-190° (Method B) [5]. In this way a simple operation gives the unsaturated ketones in 60-65% yield.

The reactions described in this paper can be readily carried out on a large scale, and they make isoprenoid alcohols completely accessible. These substances include important natural perfumes and they are of great interest in the synthesis of natural and biologically active compounds (vitamins A, E, and K; carotinoids; terpenes).

SUMMARY

A description is given of the total synthesis of the isoprenoid alcohols linalool, geraniol, nerol, nerolidol, farnesol, geranyllinalool, geranylgeraniol, and phytol and also of the intermediate products in this synthesis.

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LETTERS TO THE EDITOR

Until now the question of whether the chemisorption of nitrogen on iron catalysts for ammonia synthesis is accompanied by dissociation into atoms has remained obscure. In order to resolve this question, isotopic exchange between N_2^{14} and N_2^{15} on the following catalysts was studied under comparable conditions: 1) Fe-I, unpromoted iron; 2) Fe-II, with K_2O; 3) Fe-III, with K_2O and Al_2O_3; 4) Fe-IV, with K_2O, Al_2O_3, and CaO. On the catalyst Fe-III the rate of exchange was comparable to the rate of the catalytic decomposition of ammonia.

It was found that, for a given reduction schedule, the highest rate of exchange is observed on the unpromoted catalyst Fe-I, which is of low activity for the synthesis of ammonia. On the catalyst Fe-II, which is fairly active in ammonia synthesis, no nitrogen exchange was observed. When we take account of the fact that unpromoted iron and iron with an addition of K_2O are reduced at the same rate, the absence of exchange on the catalyst Fe-II cannot be ascribed to incomplete reduction of Fe-II. Parallel studies of isotopic exchange and decomposition of NH_3 on Fe-III showed that the temperature of the catalytic decomposition of NH_3 is 100-200° below that for the beginning of the isotopic exchange of nitrogen. If for nitrogen exchange we assume the most probable dissociation or half-dissociation mechanism, which requires breakdown of nitrogen molecules into atoms, it may be considered that our results support the view that in the catalytic process nitrogen is chemisorbed in the molecular form without breakdown into atoms.

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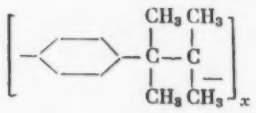
The action of organic and inorganic peroxides on organic compounds has been investigated by various authors, who have usually found dimers of the original compound among the reaction products [1,2]. Thus, Kaufman, Mark, and Mesrobian obtained 1,2-bis-p-tolylethane by the action of benzoyl peroxide on p-xylene [3].

We investigated the reaction of p-diisopropylbenzene with various organic and inorganic peroxides and found that, depending on the conditions, this reaction gives polymers of various molecular weights. The polymer obtained, which may be called poly[(tetramethylethylene)phenyl], is made up of the following structural units:



It was found also that the nature of the peroxy compound plays a very important part. The best results are obtained by the use of tert-butyl peroxide, whereas cumene peroxide gives the lowest yield of polymers. In this reaction the polymer is formed as a result of numerous acts of recombination of the radicals formed, and this process, therefore, can be justifiably called "polyrecombination." We have shown that this

method can be extended to other hydrocarbons and mixtures of hydrocarbons. Thus, preliminary experiments have shown that, under certain conditions, polymers are formed from biphenyl and also from p-xylene.

V. V. Korshak, S. L. Sosin, and M. M. Chistyakova

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CURRENT EVENTS

ALL-UNION CONFERENCE ON THE CHEMICAL PROCESSING OF PETROLEUM HYDROCARBONS IN THE PRODUCTION OF INTERMEDIARIES FOR THE SYNTHESIS OF FIBERS AND PLASTICS

An All-Union Conference on the Chemical Processing of Petroleum Hydrocarbons in the Production of Intermediaries for the Synthesis of Fibers and Plastics was held in Baku from May 27 to June 2. It was called by the Scientific and Technical Council on the Chemical Processing of Petroleum Hydrocarbons of the Division of Chemical Sciences of the Academy of Sciences of the USSR and by the Academy of Sciences of the Azerbaidzhanian SSR. The conference was devoted to a discussion of the general results of scientific investigations directed toward the development of ways of synthesizing fibers and plastics from petroleum hydrocarbons. Scientists and specialists in the petroleum and chemical industries from Moscow, Leningrad, Baku, Alma-Ata, Minsk, Sverdlovsk, Erevan, Grozny, Irkutsk, and other cities took part in the work of the conference. Thirty-five papers and communications were presented at the conference; they concerned the resources of individual hydrocarbons in petroleum and petroleum products, the methods of preparing raw material for the production of macromolecular compounds on a petroleum basis, and the methods of applying these in the preparation of new types of plastics, resins, and synthetic fibers.

In opening the conference, the President of the Academy of Sciences of the Azerbaidzhanian SSR, Academician M. M. Aliev, pointed out the importance of the subjects to be discussed.

In an introductory address, the Academician-Secretary of the Division of Chemical Sciences of the Academy of Sciences of the USSR, Academician N. N. Semenov, discussed the progress of world and Soviet science during the last 15-20 years and pointed out that an outstanding achievement in chemistry was the creation of the great variety of plastics, new materials which can now be synthesized with predetermined properties. Plastics are widely applied in various branches of industry and, in particular, in aircraft construction, in shipbuilding, in the building industry, in medicine, in agriculture, etc. We have invented, and are still inventing, synthetic rubbers that are superior in properties to natural rubber. Academician N. N. Semenov discussed also the many other extensive possibilities for the chemical utilization of petroleum, in particular the petroleums of the Azerbaidzhanian SSR, for the preparation of intermediaries for basic organic synthesis.

In his paper on "Ways of Utilizing Petroleum Hydrocarbons in the Manufacture of New Types of Synthetic Fibers," the Chief Technologist of the combine "Azneftezavod" R. G. Ismailov discussed the resources of various hydrocarbons in Azerbaidzhanian petroleums. He particularly emphasized the presence of a considerable amount of cyclohexane hydrocarbons, which are of great interest as raw material for the production of polyamide resins and synthetic fibers.

B. A. Krentsel, speaking on behalf of Academician A. V. Topchiev and himself, reported investigations on the synthesis of stereoregular polyolefins. Special attention was given to the preparation of new crystalline polypropylenes and polyisobutylenes of various molecular weights and structures.

E. D. Tulupova and Corr. Memb. Acad. Sci. USSR N. I. Shuikin discussed the results of their investigations on the isomerization of m-xylene into p-xylene in the liquid and vapor phases in presence of various catalysts. The authors showed that the isomerization of m-xylene in presence of double compounds of aluminum chloride with antimony trichloride or stannous chloride attains a state of thermodynamic equilibrium in

four hours at 100°. In the vapor phase equilibrium yields of p-xylene are obtained by the treatment of m-xylene at 450-500° in presence of gumbrin as catalyst.

A. D. Sulimov, T. V. Zhokhovskaya, and V. M. Olevsky reported results on the preparation of p-xylene from petroleum raw material by the catalytic aromatization of narrow fractions with subsequent isolation of a concentrate of C_8 aromatic hydrocarbons by azeotropic distillation with methanol. They reported also on the low-temperature separation of p-xylene from a mixture of aromatic hydrocarbons and the isomerization of the remaining mixture into p-xylene over an aluminum silicate catalyst. The yield of p-xylene in this combined process of isomerization and low-temperature crystallization is 50%, instead of the 12-14% obtained without isomerization.

Academician A. V. Topchiev, G. M. Mamedaliev, and Academician of the Acad. Sci. AzSSR Yu. G. Mamedaliev reported results on the synthesis of xylenes by the dealkylation of polymethylbenzenes and the simultaneous alkylation of toluene in presence of synthetic aluminum silicates. It was shown that in the catalytic treatment of polymethylbenzenes with toluene at 480° and 5-15 atm the yield of xylenes is 26-30% and that in their formation, not only dealkylation of the polymethylbenzenes, but also the isomerizations of m- and o-xylenes are of great importance.

Fundamentally new industrial methods for the production of caprolactam from cyclohexane were discussed by A. A. Streltsova, speaking on behalf of A. A. Artemyev, E. V. Genkina, K. S. Vulfson, F. A. Butaev, and herself. The authors emphasized that the scheme cyclohexane → cyclohexanone oxime → caprolactam showed great promise. This method has the advantage over all other known methods of manufacturing caprolactam in that the chemical steps are fewer and the process must ultimately result in substantial lowering of the cost of caprolactam.

Corr. Member V. V. Korshak, S. L. Sosin, and B. K. Krichevtsev gave an interesting paper on the preparation of dimethyl terephthalate. As a result of a study of the oxidation of p-dialkylbenzenes by atmospheric oxygen in the liquid phase the authors have found a method of carrying out the oxidation of a methyl group of p-xylene and the methyl group of p-toluic ester in one stage. This method gives dimethyl terephthalate that is purer and cheaper than that obtained by other methods.

The kinetics and chemistry of the liquid-phase oxidation of cyclohexane by atmospheric oxygen were examined in a paper by N. M. Emanuel, I. V. Berezin, and E. G. Denisov. The results are very promising for the future utilization of this process in the manufacture of such important intermediates in the polyamide-fiber industry as cyclohexanone and adipic acid. A very effective method of stimulating reaction is based on N. M. Emanuel's principle of gaseous initiation of liquid-phase chain oxidation reactions.

O. K. Bogdanova, speaking on behalf of Academician A. A. Balandin, A. P. Shcheglova, I. P. Baryshnikova, and herself, reported results of work on the effect of the structure of the hydrocarbon on the kinetics of dehydrogenation of ethylbenzene, cumene, and ethylcyclohexane. The authors showed that, in presence of a fully hydrogenated ring and in absence of conjugation, dehydrogenation of the side chain is rendered difficult. It was shown also that, in presence of the catalyst investigated, the yields of styrene and α-methylstyrene obtained at 580-600° attain 70-83% on the amount of hydrocarbon that reacts, which is of undoubted practical interest. A. P. Shcheglova, Academician A. P. Balandin, and O. K. Bogdanova investigated the catalytic dehydrogenation of isopentenes and isopentene-isopentane mixtures into isoprene and established the possibility of obtaining isoprene in yields of more than 90% on the amount of the isopentenes that reacted. A similar paper on the dehydrogenation of an isopentene-isopentane mixture into isoprene was given by Academician of the Acad. Sci. AzSSR Yu. G. Mamedaliev, M. A. Dalin, T. I. Mamedov, and A. Z. Shikhmamedbekova.

Speaking on behalf of Academician B. A. Kazansky, G. Ya. Kondratyeva, and himself, O. D. Sterligov discussed the catalytic dehydrogenation of isopentane into isopentenes over a chromium aluminate catalyst and the selection of the procedure for the analysis of the mixtures of isopentenes obtained. In the discussion on this paper, Corr. Member N. I. Shuikin stated that he, in collaboration with E. A. Timofeeva and T. P. Dobrynina, had obtained similar results on the dehydrogenation of isopentane, and also of n-pentane, in presence of a calcium chromium aluminate catalyst, which was distinguished not only by its high activity, but also by its high stability.

Academician A. V. Topchiev, I. F. Baev, Ya. M. Paushkin, and M. V. Kurashev reported a new method of alkylating benzene with propene in which a new catalyst, prepared from boron trifluoride and orthophosphoric acid, was used. The use of this catalyst makes it possible to obtain high yields not only of cumene, but also of p-diisopropylbenzene, which can serve as raw material for the manufacture of terephthalic acid.

K. V. Topchieva and A. M. Rambaeva gave a paper on "Catalytic Hydrochlorination of Acetylene," in which it was shown that this reaction can be carried out in a flow system with a nonmercurial catalyst. This method is promising and may be of industrial importance when developed.

T. I. Naryshkina and Corr. Member N. I. Shuikin reported their main results on the catalytic synthesis of cyclopentadiene and methylcyclopentadiene by the dehydrocyclization of diolefinic open-chain hydrocarbons and by the dehydrogenation of the corresponding cyclohexanes and cyclohexenes. The authors have found the optimum conditions for these reactions.

B. L. Moldavsky reported results of work on the direct oxidation of propene to acrolein in presence of a copper catalyst. This work was carried out in accordance with the unified plan of LenNII, the Institute of Physical Chemistry of the Academy of Sciences of the USSR, and NIIS.

A. N. Bashkirov, Yu. B. Kogan, and Yu. B. Kryukov described a new method of obtaining aliphatic amines from carbon monoxide, hydrogen, and ammonia.

In a paper by B. A. Kazansky, A. L. Liberman, O. V. Bragin, and G. V. Loza entitled "Catalytic Cyclization of Paraffins with Formation of Cyclopentanes" it was shown that C_7 branched paraffins can be converted into cyclopentane homologs in presence of platinized charcoal (20% Pt).

The original program was extended to include a paper by D. I. Rudkovsky on oxo synthesis and its possible use for the preparation of intermediates for synthetic fibers and plastics.

Great attention was paid to the report of the work of V. S. Aliev, A. P. Kasimova, Z. N. Tmenov, and Sh. K. Kyazimov on the catalytic dehydrogenation of propane and butane in a fluid bed of chromium aluminate catalyst and also on the pyrolysis of hydrocarbon gases in a continuous stream of coke heat-carrier.

Great interest was aroused by the papers of S. D. Mekhtiev on "Chlorination of Cyclohexane Hydrocarbons," V. G. Plyusnin on "Separation of Benzenedicarboxylic Acids," Z. G. Amerik and Orkina on "Coking Products from Heavy Petroleum Residues," and Corr. Member Acad. Sci. USSR A. D. Petrov and E. P. Kaplan on "Organomagnesium and Organolithium Synthesis of Macromolecular Cyclic Hydrocarbons." All the papers were followed by a lively exchange of views.

The conference noted that in the last few years there had been great scientific and industrial advances in the synthesis of macromolecular compounds. Experience of large-scale production of new types of polymers in capitalist countries has shown that such products encourage the development of advanced branches of technology, modern methods of building, and agriculture. The Soviet Union, with its enormous resources of raw material, teams of highly qualified specialists, and processes already ready for introduction into industry, has every possibility of rapidly catching up with the foremost capitalist countries in this new branch of technology.

The participants of the conference took part in various excursions arranged by the organizing committee. They visited oil fields, scientific research institutes, and the Sumgait synthetic rubber factory. During their ten days in Baku many of the participants shared their experience and exchanged views with representatives of research institutes and industry and established scientific and business contacts. Some visited the laboratories of the Azerbaidzhan State University, AzNII, and the Petroleum Institute of the Academy of Sciences of the AzSSR and acquainted themselves with the work being carried out. The First Secretary of the Azerbaidzhan Branch of the Communist Party of the Soviet Union Comrade I. Mustafaev and the President of the Soviet of Ministers of the AzSSR Comrade V. Ragimov took a lively interest in the results of the conference and promised to give their support to further measures for the development of research into petrochemical synthesis as a basis for the production of synthetic rubber and new types of man-made fibers. We must remark on the exceptionally courteous and attentive manner in which the leaders of the Academy of Sciences and industry of Azerbaidzhan acted toward the participants of the conference and also the exceptionally warm welcome and kind hospitality that we received from all our Azerbaidzhanian comrades.

At the closing session on May 30 the following recommendations were made.

1. Extensive development of investigations on the isolation of cyclohexane from petroleum fractions by economically advantageous methods, taking into account its great value for the preparation of substances such as caprolactam and adipic acid. In view of the presence of considerable resources of cyclohexane in most Baku petroleums, the conference considered that it was desirable to concentrate work on the isolation and purification of cyclohexane in Azerbaidzhanian scientific establishments, in which such investigations had already started.

2. In view of the great importance of the problem of finding a more economical method of preparing olefins (ethylene, propene) on the large scale and in view also of the inadequate development of research in this field, a special session of the Scientific-Technical Council is to be called for November-December 1957 for the discussion of this problem.

3. Extensive research on the electro- and thermo-cracking of C_2-C_4 hydrocarbons must be carried out.

4. In view of the importance of the method of preparing isoprene which has now been worked out under laboratory conditions, it is necessary to carry out confirmatory trials of this process in experimental plant.

5. Acceleration of completion of work on the isomerization of m- and o-xylenes into p-xylene and on the separation of xylene isomers with the object of obtaining all the data required for the planning of large-scale plants in the shortest possible time.

6. The conference noted that the development of methods of oxo synthesis and telomerization are of interest for the extension of the manufacture of various intermediates required in the production of polymeric materials.

7. It is desirable to proceed further in the work on the synthesis of alcohols and alkylamines from carbon monoxide, hydrogen, and ammonia.

8. Development of investigations on the preparation of new acrylic and methacrylic derivatives, on the preparation of α-epoxides, synthetic glycerol, and other substances on the basis of olefin oxidation, and on the hydrochlorination of acetylene with the aid of nonmercurial catalysts.

9. The Presidium of the Academy of Sciences of the AzSSR should be requested to publish the Transactions of the Conference.

The participants of the conference expressed their confidence that the conference would result in further advances in chemical processing of petroleum hydrocarbons and would help in the further extension of Soviet industry in the fields of synthetic fibers and plastics manufactured on a basis of petroleum products.

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